Guided Etching and Deposition of Transition Metal Dichalcogenides

by

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B.S. and M.S. in Materials Science and Engineering

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Abstract

Two-dimensional (2D) transition metal dichalcogenides (TMDs) with engineered nanopores have been suggested as a promising materials system in membrane and catalysis applications in both the energy and environment fields. Because of its atomic thinness, 2D-TMDs are promising candidates for osmosis energy harvesting membranes. Furthermore, the scalable nanopore preparation in MoS\(_2\) crystals provides a more cost-efficient option replacing precious metal-based catalyst for hydrogen evolution reactions catalysis. As an emerging class of semiconductor materials, 2D-TMDs have also attracted attention in electronic and optoelectronic applications, which require lithography processes to define the desired device structure. However, conventional top-down patterning methods rely on temporarily coating a polymer-based resist, which has been found challenging to remove completely and as such is detrimental to 2D devices. Development of a resist-free, guided growth of TMDs is therefore desirable.

We demonstrate the guided MoS\(_2\) nanopore formation by engineering structural defects prior to the oxidative annealing process as a scalable and parallel process susceptible to large-
scale applications. This process is based on our observation that the nanopore distribution is dramatically different in strained and unstrained MoS$_2$ crystals, which indicates that nanopore formation reflects distribution of the underlaying structural defects that act as nanopore nucleation sites. Our experimental observations indicate that dislocations in MoS$_2$ play a role in preferential nanopore nucleation. We further explore guided defect introduction by exposing MoS$_2$ crystals with electron and laser beams. By varying electron beam exposure dose prior to annealing MoS$_2$ in air, the nanopore formation density can be controlled. Laser beam exposure, as another beam-based treatment, is also observed to locally enhance the etching of mechanically exfoliated WS$_2$ under regular wet transferring protocol. Finally, we explored the guided growth on a laser exposed WS$_2$ template and on electron beam exposed dielectric substrates. We show that MoS$_2$ preferentially nucleates at laser exposed exfoliated WS$_2$ crystals, forming WS$_2$-MoS$_2$ heterostructure. We then further demonstrate that the MoS$_2$ growth can be guided to the customized pattern prepared by electron beam exposure on bare SiO$_2$ substrates.

This thesis provides insights into the role of defects during nanopore formation, and new process approaches for guided TMD etching and growth, which serve as a concept generally applicable to other 2D materials systems.

Thesis Supervisor: Professor Silvija Gradečak

Thesis Co-advisor: Professor Jing Kong

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## List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>AC</td>
<td>Armchair</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-scattered electrons</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron beam lithography</td>
</tr>
<tr>
<td>ED</td>
<td>Electrodialysis</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
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<tr>
<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>GB</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>HAADF</td>
<td>High angle annular dark field</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
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<tr>
<td>HIM</td>
<td>Helium ion microscopy</td>
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<tr>
<td>min</td>
<td>Minute</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>RED</td>
<td>Reverse electrodialysis</td>
</tr>
<tr>
<td>RPM</td>
<td>Rotation per minute</td>
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<tr>
<td>SE</td>
<td>Secondary electrons</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
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<tr>
<td>SKPM</td>
<td>Scanning Kelvin probe microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TMD</td>
<td>Transition metal dichalcogenide</td>
</tr>
<tr>
<td>vDW</td>
<td>van der Waals</td>
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<td>ZZ</td>
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Chapter 1 Introduction

Following the monumental discovery of graphene\(^1\), a single atomic layer graphite, in 2004, two-dimensional (2D) materials including transition metal dichalcogenides (TMDs) have been intensively studied due to their exceptional physical and chemical properties\(^2\text{-}^7\), with a range of new applications being proposed. For example, it is suggested that MoS\(_2\)-based field effect transistors (FET) possess superior power efficiency and on/off ratio over Si-based FET\(^8\). The benefit of using MoS\(_2\) as channel material prevails especially when the device size scaling is below 5 nm\(^9\), which causes serious short channel effect in conventional Si-based FETs. Moreover, the exceptional optical properties of TMDs enable applications including solar cells\(^10\text{-}^{11}\), photodetectors\(^12\text{-}^{13}\), and chemical sensors\(^14\text{-}^{15}\). To realize the potential applications of TMDs more scalably and controllably, the material has to be grown by large area deposition methods followed by lithography to define the targeted location and shape. Conventional lithography approaches, including photolithography and electron beam lithography, involve the deposition and removal of polymer-based resist. However, it is challenging to remove the resist from TMDs, and the residual resist could impact the device performance and quality. Thus, a growth process without having to use resist is desirable.

In search of a sustainable future, air pollution, climate change and energy security have raised paramount attention. Nanoporous MoS\(_2\) has been proposed as a potential candidate for future renewable energy material, including energy harvesting\(^16\), energy conversion\(^17\) and energy storage\(^18\). In this thesis, we explore the scalable pore formation approaches for membrane and catalysis applications. As a scalable and resist-free treatment for guided
nanopore formation, defect engineering is the strategy used in my thesis.

In the first part of this chapter, fundamental structure and properties of TMDs will be introduced. Then, potential applications of resist-free guided addition/subtraction processes for TMDs are summarized and discussed. Finally, the drawbacks of conventional patterning processes that motivated my thesis work are discussed.

1.1 Structure of Transition Metal Dichalcogenides

1.1.1 Crystal Structure and Nanopore Configuration

2H phase of the TMD family members (MoS₂, WS₂, MoSe₂, WSe₂, etc.) share the same crystal structure. The crystal structure of 2H-MoS₂ was first determined by Dickinson and Pauling in 1923¹⁹. As illustrated in Figure 1-1 (a), the transition metal atom M (Mo, W) and chalcogenide atoms X (S, Se) form honeycomb structure. Two primitive vectors, \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \), are defined in Figure 1-1 (a), forming a unit cell of 2H-MX₂. In bulk MX₂, M and X atoms are chemically bonded within one layer, while the stacked layers are bonded by van der Waals forces, as illustrated in Figure 1-1 (b), in which the third primitive vector, \( \mathbf{c} \), is defined. With the known interlayer distance (6.5 Å), one can determine the number of layers of MX₂ by its thickness.
Shape of 2D TMDs reflect their crystal symmetries, same as 3D crystalline materials. Because the crystal and pore shapes are determined by edge energy, we could verify the observed preferential edge orientation by evaluating corresponding edge energy in major crystal orientations. The edge energy associated to different edge types in TMD monolayers is anisotropic. Two major edge orientations in the MX₂ structure are illustrated in Figure 1-2 (a), namely zigzag (ZZ) and armchair (AC). To compare the edge energy, one can evaluate the number of dangling M-X bonds per unit length for both ZZ edge and AC edge, assuming negligible edge reconstruction and constant dangling bond energy in both cases. The edge energy of a ZZ edge is 2.00 dangling bonds per unit cell vector (length of a₁), while the edge energy of an AC edge is 2.77 dangling bonds per unit cell vector. Other edge types in random orientation yield even higher edge energy. Therefore, the most favorable configuration is ZZ edge, which minimizes the edge energy. ZZ edges are preferred during both growth (material addition) and decomposition (material subtraction) processes of monolayer MX₂ materials, which is confirmed by experimental results of ZZ edge TMD crystals²⁰–²² as well as ZZ edge nanopores in MoS₂²³,²⁴.
The shape of MX$_2$ crystal and the nanopore in MX$_2$ is determined by the edge energy, same as the determination of bulk crystal shape$^{25}$. Based on our discussion above, the preferred edge orientation is ZZ. There are two types of ZZ edges: X-ZZ and M-ZZ, as illustrated in Figure 1-2 (a). The preferred MX$_2$ crystal shape is hexagonal if X-ZZ and M-ZZ are equally stable; if the growth condition favors M-ZZ edges, as illustrated in Figure 1-2 (b), both the MX$_2$ crystal and the nanopore in it are of triangular shape, with the nanopore (or antidots) edges align along M-ZZ.

Figure 1-2 (a) Zigzag and armchair edges of MX$_2$. (b) Nanopore configuration in monolayer MX$_2$ crystal model. Blue: transition metal; yellow: chalcogen. Variants of zigzag (ZZ) and armchair (AC) are illustrated as six blue and red arrows, respectively.

1.1.2 Structure of Defect Species in TMD

Similar to bulk materials and other materials, non-zero defect concentration present in TMD crystals at above 0 K temperature due to the entropy term in total free energy. Here, for the convenience of discussion, we take MoS$_2$ as an example material system. A sulfur vacancy ($V_s$) is a point defect with a missing S atom, while a disulfur vacancy ($V_{s2}$) is a defect with
two missing S atoms. Similarly, $V_{\text{MoS}_3}$ and $V_{\text{MoS}_6}$ can occasionally be found. An Mo atom can replace two sulfur atoms, forming $\text{MoS}_2$; similarly, two sulfur atoms can replace an Mo atom, forming an $S_{2\text{Mo}}$. Figure 1-3 shows six common different point defects observed in scanning transmission electron microscopy (STEM) of single-layer (1L) MoS$_2$.

![Figure 1-3](image)

Figure 1-3 STEM-ADF (annular dark field) image of point defects in 1L-MoS$_2$.

In addition to the point defect species discussed in Figure 1-3, the ones with more lattice distortion have also been observed in TMD crystals. For instance, dislocation can also be observed in TMD crystals. Different structures of 5|7 dislocations, which consist of a 5-member ring and a 7-member ring, are illustrated in Figure 1-4 (a). Similar to edge dislocations in bulk materials, 5|7 dislocations in 2D TMDs can be viewed as cores separating one side with missing array of atoms along armchair (AC) direction and the other with a pristine configuration (Figure 1-4 (b)). 5|7 dislocations have the shortest possible Burgers vector, $\mathbf{b} = <1, 0>$. The gliding direction of a 5|7 dislocation lies along zigzag direction (ZZ), while the climbing direction is aligned along AC. A 4|8 dislocation, on the other hand, is
associated with Burgers vector $\mathbf{b} = <1, 1>$, with gliding direction along AC. A 6|8 dislocation is derived from a metal polar 5|7, by adding two sulfur atoms between the original five-member ring and seven-member ring (Figure 1-4 (c)\textsuperscript{27}, upper panel), while 4|6 dislocations are formed by removing two sulfur atoms from sulfur polar 5|7 dislocations (Figure 1-4 (c), bottom panel).

![Dislocation structure in MX2](image)

Figure 1-4 Dislocation structure in MX$_2$. (a) Structure of metal polar (left), sulfur polar (right) 5|7 dislocations and 4|8 dislocation (center)\textsuperscript{27}; (b) atomic structure of 5|7 dislocations in MX$_2$\textsuperscript{28}; (c) 6|8 dislocation (top) and 4|6 dislocation (bottom).\textsuperscript{27} Blue atoms: M; yellow/orange atoms: X.

The dislocation structure in 2D materials such as graphene, hexagonal boron nitride (h-BN, Figure 1-4 (b)), and TMD is a 2D analogy of edge dislocation in bulk crystalline materials.
To illustrate, the structure of an edge dislocation in simple cubic crystal is shown in the ball-stick model\textsuperscript{29}, Figure 1-5 (a), which could be interpreted as a perfect three-dimensional (3D) cubic lattice missing half plane of atoms. The lattice is therefore distorted, inducing compressive (tensile) strain in the upper (lower) half of the crystal. One can construct a dislocation starting from a perfect 2H-MX\textsubscript{2} lattice using the same concept for edge dislocation in 3D crystals discussed above. First, as shown in the shaded area of Figure 1-5 (b), half line of atoms is removed from perfect MX\textsubscript{2} crystal. Then, stitch the lower half of the MX\textsubscript{2} crystal to reconstruct a continuous 2D lattice (Figure 1-5 (c)). Finally, one can construct a 5|7 dislocation introducing compressive (tensile) strain in the upper (lower) half of the crystal, as depicted in Figure 1-5 (d). Here, we define \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) as unit vectors of the 2H-MX\textsubscript{2} crystalline lattice.

One can then use the same convention for determining the Burgers vector of a dislocation in 2H-MX\textsubscript{2} crystals, as in their 3D cubic counterpart. If the circuit formed encloses the dislocation core, an extra displacement \( \mathbf{b} \) is needed to close the circuit in Figure 1-5 (e) (formed by black arrows and \( \mathbf{b} \)): 

\[
-4\mathbf{a}_1 - 4\mathbf{a}_2 + 4\mathbf{a}_1 + 4\mathbf{a}_2 + \mathbf{b} = 0.
\]

Otherwise, the circuit closes itself without any extra term (blue arrows).
Figure 1-5 Construction of dislocation in 2H-MX$_2$ crystalline structure. (a) An edge dislocation in simple cubic lattice. (b) Perfect 2H-MX$_2$ crystalline lattice. The shaded half line of atoms is removed. (c) Stitch the half atomic line together to reconstruct a continuous 2D lattice. (d) Final 5/7 dislocation structure. $a_1$ and $a_2$ are unit vectors of the 2H-MX$_2$ crystalline lattice. (e) The convention for measuring Burgers vector $b$ by forming a circuit enclosing the dislocation core. Ball-stick model in (a) is adapted from Ref. 29$^{29}$.

Line defects such as grain boundaries (GB) in single layer TMD crystals have been observed$^{30}$. As illustrated in Figure 1-6 (a), an array of dislocations on WS$_2$ GB can be resolved in the STEM-ADF image. The dislocations in WS$_2$ are found to be highly mobile at room
temperature and low e-beam energy (80 kV) in TEM. Interestingly, instead of keeping the same structure, these dislocations may evolve between 6|8 and 4|6 during the dislocation motion.

Mirror twin boundaries, another type of line defect, can also be found in single layer MoS$_2$. The atomic structure of a mirror twin boundary is depicted in Figure 1-6 (b), where 8-4-4 rings form a chain along the boundary. The energies of GBs as a function of tilt angle is calculated and plotted in Figure 1-6 (c), with GBs formed by 5|7 or 4|8 dislocation array. 4|8 dislocations are energetically more favored and more likely to be found in GBs with tilt angle higher than 45°.

Figure 1-6 Line defects in TMD crystals. (a) 22° grain boundary found in 1L-WS$_2$; (b) Structure of mirror twin grain boundary in 1L-MoS$_2$; (c) dependence of grain boundary energy on inter-grain misorientation (curves and data points).
1.2 Applications of 2D Devices

Reverse Electrodialysis

To address the issue of global warming and energy security, renewable and sustainable energy sources have been researched and developed for decades. In contrast to solar, wind, and hydropower energies, the ocean is a largely untapped renewable and clean energy source. Energy can be extracted from the process of mixing sea water and fresh water because of the free energy associated with their mixing. One of the techniques for extracting salinity gradient energy is reverse electrodialysis (RED), which is the reverse process of desalination. When sea water is desalinated, energy is provided to force the separation of salt and fresh water. This process is called electrodialysis (ED). RED, on the other hand, extracts energy from the mixing of sea water and fresh water.

To realize RED, membrane materials that preferentially allow either cation or anion to pass are required. This behavior is called ionic rectification. A simplified RED cell is shown in Figure 1-7. A typical RED cell consists of alternating anion and cation exchange membranes (AEM and CEM). As a result, there is a net cation flow to the cathode and a net anion flow to the anode. The charge neutrality is compensated by the redox reaction at the electrodes. The electrons collected from the anode thus provide electrical power to the external circuit.
MoS$_2$ has been recently demonstrated as a promising candidate for RED membrane material. Nano-power generators using single-layer MoS$_2$ with a single nano-sized pore (10-25 nm) have demonstrated extraordinary potential for high areal power densities compared to conventional membrane materials$^{16}$. The power density, which linearly scales with the number of pores in MoS$_2$, was calculated to be 1 MW/m$^2$$^{16}$. In this demonstration, however, only one pore on a single-layer MoS$_2$ was formed by electron beam drilling in a transmission electron microscope (TEM). In other words, estimated 1 MW/m$^2$ would be achieved for a membrane with porosity of 30% and 10 nm pore sizes.

Membrane conductance is one of the parameters that governs the performance of an RED cell. As discussed earlier, multiple nanopores on the membrane act as parallel resistors, yielding maximized total conductance. Another method of maximizing the output current of the RED cell is to maximize the ionic conductance of each nanopore. The pore conductance is
described as the following form$^{33}$:

$$
G = \kappa_b \left[ \frac{4L}{\pi d^2} \frac{1}{1 + 4 \frac{l_{Du}}{d}} + \frac{2}{\alpha d + \beta l_{Du}} \right]^{-1}; \quad l_{Du} = \frac{\vert \Sigma \vert / e}{2c_s}
$$

where $L$ is the pore length, $d$ is the pore diameter, $l_{Du}$ is the Dulkin length, $\kappa_b$ is the bulk conductivity, $\Sigma$ is the surface charge, $c_s$ is the salt concentration, $e$ is the elementary charge, $\alpha$ is the geometrical factor and $\beta$ is the fitting factor. According to Equation 1-1, the shorter (thinner) pores with larger diameter are more desirable because of the lower pore resistance.

A single-layer graphene (thickness $\sim 3.1\,\text{Å})^{34}$ is thinner than a single-layer TMDs ($\sim 6.15\,\text{Å}, \text{MoS}_2)^{35}$, so graphene has lower pore resistance if other variables are kept constant. However, TMDs membranes are more compatible with aqueous solution. Due to the polar nature of the bonding between Mo and S, MoS$_2$ nanopore membranes have been found to have better water/ion transport than graphene membranes, which are highly hydrophobic and require functionalization or surface modification to alleviate this issue$^{36,37}$.

A typical I-V output plot of a MoS$_2$ membrane in a fixed salt concentration is shown in Figure 1-8 (a)$^{38}$. The conductance of the membrane increases as the diameter of the pore increases. The pH of the solution also has an impact on pore conductivity, as shown in Figure 1-8 (c). In this case, higher pH enhances the pore conductance and this suggests that we can modulate the surface charge around the nanopores by tuning the pH in the solution$^{38,39}$.
Figure 1-8 Dependence of pore conductivity on (a) pore size; (b) salt concentration; (c) pH. Pore size: Δ:25nm; □:6nm; ○:2nm. RED cell voltage is another factor determining its output power. The cell voltage, $V_{diff}$, can be described as the Equation 1-2:

$$V_{diff} = S(Σ)_{ls} \frac{RT}{F} \ln \left[ \frac{a_{cis}^{KCl}}{a_{trans}^{KCl}} \right]$$

where $S(Σ)_{ls}$ is the ion selectivity ($0 < S < 1$, for ideal ion selectivity, $S = 1$), $a^{cis}$ and $a^{trans}$ are salt activity (concentration) in cis/trans sub-cell, respectively, $F$ is the Faraday constant, $T$ is the temperature, $R$ the is gas constant. Although the cell voltage can be enhanced by increasing the salinity gradient, this parameter should be considered as constant for practical application ($\sim 10^3$). To maximize the voltage, the ion selectivity of the membrane materials, $S(Σ)_{ls}$, should be maximized. A smaller pore size yields a higher surface charge $Σ$, which boosts $V_{diff}$. According to Equation 1-1 and 1-2, an optimized pore size can be found by considering both $G$ (larger $d$ is favored) and $V_{diff}$ (smaller $d$ is favored).

To go beyond single pore formation and to generate pores in 2D TMD membrane material for practical applications, repeatable, reliable, and parallel processing is required. From the etching behavior of bulk materials, we know that etchant chemicals preferentially attack
material defects, such as grain boundaries\textsuperscript{41} and dislocations\textsuperscript{42}. Thus, the mechanism of nanopore formation in 2D-TMDs by oxidation should be closely related to defects in the material. In Chapter 3, defect-mediated nanopore formation is used as a resist-free approach of guided MoS\textsubscript{2} removal.

**Catalysis for Hydrogen Evolution Reaction**

Due to the high active site to mass ratio, nanostructured MoS\textsubscript{2} has been studied and proposed\textsuperscript{17,43,44} as a promising candidate for catalyst of hydrogen evolution reaction (HER, Figure 1-9), which is critical for water-splitting process in energy conversion and storage. Conventionally, precious metal such as Pt provides decent HER catalyzing performance, but the device cost has been an issue of commercializing the technology. It has been experimentally confirmed\textsuperscript{45} that the HER rate scales with the edge length, not the area of MoS\textsubscript{2} crystals. Therefore, one could engineer the nanostructure of monolayer MoS\textsubscript{2} crystals to maximize the number of active sites, by introducing nanopore arrays in monolayer MoS\textsubscript{2}. The scalable processes and defect engineering technique reported in Chapter 3 and Chapter 4 would contribute to this field by providing potential path of process development for commercializing MoS\textsubscript{2}-based HER technologies.

![HER on nanostructured MoS\textsubscript{2}](image)

Figure 1-9 HER on nanostructured MoS\textsubscript{2}\textsuperscript{17}, with the MoS\textsubscript{2} crystal edges acting as catalysis active site for hydrogen evolution.
**Field Effect Transistor, FET**

The advancement of the transistor architecture has been the driving force behind the improvement of performance and power efficiency of integrated circuits in computer chips. Currently, one of the most challenging issue of conventional silicon-based FET scaling is the short channel effect, and semiconducting TMD materials, such as MoS$_2$, are promising candidates for new channel material to overcome the obstacle of continuation of Moore’s Law. Scalable processes of TMD crystals, including chemical vapor deposition (CVD, discussed in Section 2.1.2) is essential for large-scale device fabrication. To define the channel area of the FET, top-down, channel-first approach starting from wafer-scale TMD crystals followed by photolithography has been reported$^{46}$. In the next section of this chapter, the principles and the challenges of patterning TMDs by conventional lithography processes are discussed.

**1.3 Conventional Patterning Processes: Drawbacks for TMDs**

The fabrication of electronic and optical devices requires patterning processes to define the desired circuits. As shown in Figure 1-10 (a), conventional top-down patterning methods on coating a polymer-based resist (Step 1 in Figure 1-10 (a)) that is then exposed (by photons or electron beams) and developed (Step 2). The material beneath the patterned resist is selectively protected (Step 3) from the reactive etching reagent (wet etching) and/or high-energy ions (dry etching). After the subsequent selective etching of materials, the protective resist has to be removed (Step 4). Each of these steps adds to the process complexity, and in the case of 2D materials, potential materials damage$^{47,48}$. Further, residual resist is detrimental to 2D devices, and several attempts of cleaning the surfaces of 2D materials have been
reported\textsuperscript{47–49}. Lift-off approach (Figure 1-10 (b)), which frequently used in electron beam patterned metal films, is not compatible with 2D TMDs, due to its weak van der Waals interaction with substrates.

![Figure 1-10 Process flow of conventional lithography. (a) Selective protection approach realized by resist-last strategy; (b) Lift-off approach realized by resist-first strategy. The unwanted part of the film is removed when the resist is dissolved.](image)

The aforementioned issues could be avoided by source-drain (S/D) first approach, in which the source and drain (poly-Si) edges serve as nucleation sites for CVD-MoS\textsubscript{2}. However, removing the unwanted MoS\textsubscript{2} crystals at other S/D edges is necessary when integrating multiple devices. Results demonstrated in Chapter 4 provide a promising solution to the issues mentioned in this section.
1.4 Thesis Overview

This thesis demonstrates resist-free, guided TMD addition and subtraction processes, and proposes the underlying mechanism governing these approaches. Chapter 2 introduces experimental methods used in the following chapters, including sample preparation, material characterization and charged beam exposure. In Chapter 3, guided TMD etching is demonstrated by strain effect on nanopore formation MoS$_2$, along with the proposed mechanism of explaining the unusual spatial nanopore distribution in strained CVD-MoS$_2$. In Chapter 4, we show that one can modulate the areal nanopore density by electron beam exposure prior to annealing MoS$_2$ in air, followed by introducing defects by laser exposure on exfoliated WS$_2$ crystals. Electron-beam-based substrate modification is introduced in Chapter 5 to realize the guided MoS$_2$ deposition on SiO$_2$ substrates. Chapter 6 summarizes results and contribution of this thesis, followed by potential future work that expands the concepts presented and discussed in this thesis.
Chapter 2 Experimental Methods

In this chapter, experimental methods are outlined into three sections: sample preparation, sample characterization and substrate charging. Section 2.1 focuses on various TMD preparation techniques, along with their advantages and limitations for different purposes. In Section 2.2, characterization techniques used in my thesis are introduced and discussed, including Raman spectroscopy, atomic force microscopy (AFM), scanning Kelvin probe microscopy (SKPM) and scanning electron microscopy (SEM). Principles of sample charging effect and equipment features are summarized in Section 2.3.

2.1 Sample Preparation Techniques

2.1.1 Mechanical Exfoliation

As discussed in Chapter 1, TMD properties are thickness-dependent, which can be engineered by isolating crystals with various thickness. Thanks for the weak vdW interaction between each layer, one can prepare TMD crystals with desired thickness by top-down, Scotch-tape method in the laboratory, as follows. Exfoliated MoS$_2$ is prepared by first using thermal-released tape to exfoliate a small amount of MoS$_2$ from bulk crystal. The procedure is repeated 3-5 times and then a PET film was attached to the thermal-released tape to further reduce the MoS$_2$ thickness. Finally, the film is detached from the thermal-released tape and applied to the pre-cleaned Si/SiO$_2$ substrate.

There are several drawbacks of the mechanical exfoliation. First, the nature of this approach is stochastic. The size, shape and thickness of the crystals are not repeatable. The
crystals scatter randomly on the substrate, so crystal transferring would be necessary if the goal is to prepare heterostructures or fabricate source-drain-first devices. This limits the exfoliation approach beyond laboratory applications. Moreover, the residual glue on the substrate/crystal can be detrimental for the subsequent processes\textsuperscript{50}, which limits the device performance.

2.1.2 Chemical Vapor Deposition, CVD

In contrast to mechanical exfoliation discussed in the previous section, CVD of MoS\textsubscript{2} is more controllable and scalable\textsuperscript{51,52}. CVD is a deposition technique supplying precursors so that the chemical reaction takes place near or on the substrate at controlled temperature. Therefore, the desired material properties depend on CVD process parameters, including precursor type, precursor amount, substrate temperature profile, carrier gas type, carrier gas flow rate and system pressure.

CVD-MoS\textsubscript{2}

In this thesis, powder-form MoO\textsubscript{3} and sulfur are chosen as precursors for MoS\textsubscript{2} CVD process. The precursors are first vaporized by heating the powder-based precursors, then transferred toward the substrate by argon, which is chosen as the carrier gas for the growth in the thesis. Because the vapor pressure is a function of the precursor melting point, the process temperature window for the individual precursor is distinct from each other. For MoO\textsubscript{3}, the temperature is controlled near, but below its melting point (802 °C). Therefore, the range of MoO\textsubscript{3} temperature for CVD-MoS\textsubscript{2} is 650 ~ 800 °C \textsuperscript{53–56}. For sulfur, the temperature is generally above its melting point, but well below its boiling point. The range of sulfur
temperature for CVD-MoS\textsubscript{2} is generally between 100 °C and 200 °C\textsuperscript{51,57,58}. Alternatively, to lower the growth temperature of TMDs, one may choose organic-based precursors, such as metal carbonyls (e.g. Mo(CO)\textsubscript{6}), diethyl sulfide ((C\textsubscript{2}H\textsubscript{5})\textsubscript{2}S) and dimethyl selenide ((CH\textsubscript{3})\textsubscript{2}Se)\textsuperscript{59,60}, which have been used for metal-organic chemical vapor deposition\textsuperscript{61} (MOCVD). High reactivity of these precursors is the reason why lower temperature is sufficient to overcome the activation energy of TMD formation.

To prepare the substrate for CVD-MoS\textsubscript{2} growth, 6-inch p-type silicon wafer (University Wafer, sheet resistance 1 - 10 Ω/sq) with 300 nm SiO\textsubscript{2} was cleaved into 1.5 cm × 1.5 cm chips, and then cleaned following the substrate cleaning protocol: 5 min sonication in deionized (DI) water, 5 min sonication in methanol, 5 min sonication in DI water, and piranha solution (3:1 volume ratio mixture of H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{2}O\textsubscript{2}) for 40 min followed by 5 min sonication in DI water. The substrate was then placed faced-down directly on the MoO\textsubscript{3} crucible. 15 mg of MoO\textsubscript{3} precursor (Sigma-Aldrich, 99.5%) and 1.2 g of sulfur precursor (Sigma-Aldrich, 99.5%) loaded in separate alumina crucibles were inserted into a 1-inch quartz tube, in which the temperature is controlled by a single zone furnace.

The hardware setup of the CVD furnace is illustrated in Figure 2-1. New 1-inch or 3-inch quartz tubes were annealed at 1000 °C with 200 sccm Ar flow for 3 h (dummy annealing), along with new alumina boats (if any), to remove the residues in the tube before the first CVD process. The mass transport of the precursors during MoS\textsubscript{2} growth is assisted by controlling the flow of argon (Airgas, 99.5%), which acts as the carrier gas. The temperature ramp-up rate is set at 20 °C/min, and the growth temperature was at 795 °C, which is measured by a built-
in thermocouple. The parameters above were chosen based on our growth optimization, considering the crystal size, nucleation density and repeatability. The parameters can be modulated based on the desired purpose, as will be discussed in Chapter 3 (slower cooling rate) and Chapter 5 (lower growth temperature). The integrated thermal couple in the CVD furnace reflects the temperature of the MoO$_3$ crucible, whereas the temperature of the sulfur crucible is controlled by the varying the crucible distance from the hot zone. The position of the crucibles is controlled to maximize the growth repeatability. In our best-known recipe, the MoO$_3$ crucible is placed at 19 cm from the edge of the furnace, and the best position sulfur crucible after insertion is recorded after optimization.

Figure 2-1 Single-zone CVD equipment setup. Al$_2$O$_3$ boat loaded with MoO$_3$ powder is placed at the center of the hot zone, while the boat loaded with sulfur powder is placed out of the hot zone. Sulfur is inserted by sliding the magnet when the temperature reading reaches the target.

When the temperature reaches the target, the sulfur boat is inserted by sliding the magnet from the cold zone to the position defined by the recipe, which is optimized to control the timing and the amount of sulfur supply. Finally, the furnace is cooled down by opening the furnace lid. After the process, the sulfur in the boat is completely consumed, whereas the MoO$_3$ powder is transformed from light blue powder to dark purple/dark blue chunk. The MoO$_3$ residue is then removed from the alumina boat before the next growth.
2.1.3 Crystal transferring process

Crystal transferring of 2D materials is widely used when it is desirable to change the substrate environment, such as TEM sample preparation, preparing vertical heterostructures, and electrical device fabrication. The concept of crystal transferring process is illustrated in Figure 2-2. (1) A piece of “tape” is attached to the crystal, as a temporary substrate for handling the crystal with ease. (2) The whole sample is put in SiO₂ etchant to detach the crystal attached to the tape from the original substrate. (3) The crystal is then placed on top of the target substrate. (4) The temporary tape is removed from the crystal.

![Figure 2-2](image.png)

Figure 2-2 Step-by-step illustration of crystal transfer process. After the tape is attached to the sample (step 1), the underlying SiO₂ layer is removed by KOH (step 2). The tape with crystals to transfer is then placed on the new substrate (step 3). Finally, the tape is removed from the new substrate (step 4).

Poly(methyl methacrylate), PMMA, is widely used as the temporary substrate material for transferring process of 2D materials. We applied PMMA for TEM sample preparation in this thesis. First, 950K molecular weight PMMA is spin coated on the sample, with spin speed at 3000 round per minute (RPM) for 1 min. To remove the residual solvent of PMMA, the sample
is then annealed on a hotplate at 70 - 180 °C for 2-5 min. To further provide mechanical support, mechanical exfoliation tape (e.g., Nitto SPV 224PRM or Nitto 3195MS) is then applied to the exposed surface of the PMMA. Prior to its application, a small window is cut in the tape (Figure 2-3 (a)) and the tape is placed such that the target sample is centered within the window. This window eases the PMMA removal process in the fourth step (Figure 2-3 (b)).

Figure 2-3 Photographs of (a) transfer step 1 (i.e., aligned placement of tape on the substrate) and (b) transfer step 3 (i.e., aligned placement of crystal/tape structure on new TEM grid substrate).

The second step involves detaching the sample from the original substrate by using strong basic solution to etch the SiO₂. 1 M KOH is used at room temperature overnight, or at 70 °C for 2-3 h. The Si substrate is then detached from the tape, sinking to the bottom of the beaker. The tape with the sample, on the other hand, floats on the surface of the KOH solution.

For TEM sample preparation, 3 mm Cu grids (Ted Pella, #609) with holey carbon is used as the target substrate for transferring. Because the Cu grids are not electron beam transparent, the crystal has to be placed at the space in between the Cu grids, which requires precise sample
manipulation. The tape with PMMA mounted sample is mounted on the metal arm of a home-built X-Y-Z sample micromanipulator. The metal arm is then put between the long working distance lens of the optical microscope and the Cu grid on an integrated mini-hotplate. By using the live optical image and the sample manipulator, the crystal is placed at the center of the square space, as shown in Figure 2-4 (b). The sample is then carefully placed on the holey carbon by using the Z-knob. The PMMA is heated by the mini-hotplate so that the PMMA temperature surpasses the glass transition temperature, which could be confirmed by the contrast in the live optical image. Finally, the PMMA is removed from the Cu grid by carefully placing the grid in acetone for 3 h.

![Figure 2-4](image)

Figure 2-4 (a) X-Y-Z sample micromanipulator. (b) optical image of a crystal transferred onto Cu TEM grid with micron-scale precision.
2.2 Characterization Techniques

2.2.1 Raman spectroscopy

Based on the photon-phonon interaction, Raman spectroscopy provides the lattice vibration information in the sample, both for molecular form and material form. In Raman spectroscopy, a stable laser source with known wavelength is used. There are three types of photon interaction with the sample: Rayleigh, Stoke, and anti-Stoke scattering, as illustrated in Figure 2-5 (a). Most of the scattering events between the incident photon and the material are elastic, in which the final photon energy is the same as the energy of incident photons. The inelastic scattered photons induced by the vibrational level transition is measured and recorded. If the energy is transferred from the photon to the material, then the process is called Stokes transition; if the energy is transferred from the material to the scattered photon, then it is called Anti-Stokes transition. The two vibrational modes of MoS$_2$, E$_{2g}^1$ and A$_{1g}$, are listed in Figure 2-5 (b).

![Figure 2-5](image)

Figure 2-5 (a) Modes of photon interaction with the material. (b) Schematic of relevant vibrational modes in MoS$_2$.

For the purpose of this thesis, Raman data was collected at Horiba LabRam HR800
(Institute for Soldier Nanotechnologies, ISN, Figure 2-6) confocal Raman system with laser wavelength at 532 nm and 633 nm. The spatial resolution of LabRam HR800 is limited by its laser beam size, which is about 1.5 μm in diameter. During the measurement, the sample is exposed in laboratory atmosphere at room temperature. The intensity modes for a given laser are 100%, 50%, 25%, 10%, 1%, 0.1% etc. To prevent unwanted damage to the sample during measurement, the laser power was controlled at 0.93 mW and 1.22 mW for 532 nm and 633 nm, respectively (both are 10% laser intensity). All Raman data were collected at room temperature and atmospheric pressure.

Figure 2-6 Horiba LabRam HR800, ISN, MIT.

The relative Raman vibrational mode intensity depends on the wavelength of the incident laser. An example of typical Raman spectrum collected from the same MoS$_2$ crystal is shown in Figure 2-7. The Raman peak at 228 cm$^{-1}$ is assigned to the defect related vibrational mode (LA mode), which has been used to characterize the defect density of MoS$_2$,$^{63-66}$ because simple, monotonic correlation between the bombarding ion dose and the relative LA Raman mode intensity has been consistently observed.
Resonance Raman spectroscopy is used to characterize vibrational modes with small Raman intensity. As shown in Figure 2-7, the intensity of 228 cm\(^{-1}\) Raman mode is enhanced when the excitation laser is 633 nm, comparing to the one when the laser is 515 nm. The B excitonic transition energy of monolayer MoS\(_2\) is 1.98 eV\(^{67}\), which is very close to the photon energy of 633 nm laser (1.96 eV). Therefore, instead of regular Raman spectroscopy with 532 nm laser, resonance Raman with 633 nm laser is used in my thesis to improve the signal-to-background ratio of LA vibrational mode.

![Figure 2-7 Difference of regular Raman and resonance Raman spectroscopy. Green: Raman spectra taken with a 514.5 nm laser; red: Resonance Raman spectra taken with a 632.8 nm laser.\(^{68}\)](image)

With the integrated x-y motored sample stage connecting to LabSpec 6 software, LabRam HR800 is capable of taking Raman mapping data with customized measurement area, location and dwell time of Raman measurement. For each given (x, y) coordinate, a Raman spectrum is recorded. The result can be visualized by setting the intensity integration range in LabSpec.
5. For Raman measurement, the laser power is chosen so that the signal to noise ratio is optimized (preferring higher power), without damaging the sample (preferring lower power). Therefore, the laser power is generally 1 % - 10 %, and the dwell time is 3 - 5 s for Raman measurement.

By choosing longer dwell time and laser power, the lasers of LabRam HR800 can also be used for intentional laser exposure (Section 4.3) on the samples. In this mode, the laser power is set at 100 % and the dwell time is 10 s for each point.

### 2.2.2 Atomic Force Microscopy (AFM)

AFM images were collected in Veeco Dimension 3100 Scanning Probe Microscope (provided by Institute for Soldier Nanotechnologies, ISN, Figure 2-8) in ambient condition. Topographic characterization was carried out in tapping mode, in which the cantilever is oscillated near its resonant frequency. As shown in the hardware setup (Figure 2-8, right panel), the laser beam and the photo diode are used to detect the vibration of the cantilever.

The force between the sample and the cantilever is a function of tip-sample distance, which modulates the resonance frequency because the equivalent force constant of the cantilever is modulated by sample topography during scanning. There is an offset of cantilever amplitude from the original setpoint, due to the resonant frequency shift. The amplitude signal is then used to feedback the piezo to keep the cantilever amplitude constant, during which the piezo profile is recorded. (AFM, tapping mode)
2.2.3 Scanning Kelvin Probe Microscopy (SKPM)

Surface potential images discussed in Chapter 4 were collected using SKPM mode of Asylum Research Cypher AFM system, as shown in Figure 2-9. To minimize the unwanted noise from the environment, the equipment is mounted on a vibration isolation stage. SKPM is a characterization technique probing the work function, which is capable to reflect the charge trapping phenomena in dielectric materials. The sample is mounted on a steel plate, which is fixed on the magnetic chuck driven by a built-in x-y motor. Due to the limitation of the stage size, the sample has to be smaller than 1.5 cm × 1.5 cm.
Figure 2-9 Asylum Research Cypher AFM system mounted on a vibration-isolation stage, which minimizes the noise from the environment.

We use Pt coated cantilevers (MikroMasch DPE-XSC11, resonant frequency: 80 kHz; force constant: 2.7 N/m, length: 210 µm) for SKPM measurements. The closed-loop feedback, two-pass mode illustrated in Figure 2-10 is used in all of our measurements. During the measurement for each horizontal scan line, (1) the surface topography is recorded with regular “tapping” AFM mode. Then (2) the conductive cantilever is lifted away from the sample in z-direction for tens of nanometer (defined as $h$ in Figure 2-10 (a)) for the “nap” mode scan, plus the feedback from the surface profile measured in (1). The distance between the cantilever is therefore kept constant, which eliminates the unwanted cross-talk from the distance effect. In the “nap” mode, the cantilever is biased consisting of DC term ($V_{DC}$) and AC term ($V_{AC} \sin(\omega t)$):

$$V = (V_{DC} - V_{CPD}) + V_{AC} \sin(\omega t)$$

2-1

where $V_{CPD}$ is contact potential difference, which originates from the work function mismatch between the conductive cantilever and the sample. As shown in Figure 2-10 (b), an extra term
of interaction between the cantilever and the sample is due to the electrostatic force, which could originate from the work function mismatch or trapped charge in the sample. The interaction force, $F_{el}$, modulates the resonance frequency of the cantilever, thereby perturbs the cantilever vibration amplitude, which is amplified and recorded by the laser reflection of the cantilever tip. There are three separate terms of the force $F_{el}$,

$$F_{dc} = \frac{\partial C}{\partial z} \left[ \frac{1}{2} (V_{dc} - V_{CPD})^2 + \frac{V_{ac}^2}{4} \right],$$

$$F_{\omega_{ac}} = \frac{\partial C}{\partial z} (V_{dc} - V_{CPD}) V_{ac} \sin(\omega_{ac} t),$$

$$F_{2\omega_{ac}} = -\frac{\partial C}{\partial z} \frac{V_{ac}^2}{4} \cos(2\omega_{ac} t).$$

where $C$ is capacitance of cantilever-sample system, and $z$ is cantilever height relative to the sample surface. The feedback system then applies a bias, $V_{DC}$, which cancels the effect mentioned above, so that the interaction force and the amplitude offset is minimized.

SKPM data collected from Cypher AFM was analyzed in Asylum Research data management software (Version 13.17.101), an Igor module integrated with hardware controlling interface. The surface potential images were exported in the same software, with $512 \times 512$ image resolution.
Figure 2-10 Principles of SKPM. (a) Closed loop feedback mode with tapping mode for the first scan and nap mode for the second scan on the same line. (b) Schematic diagram of the force origin and the work function difference between the cantilever and the sample. 

2.2.4 Scanning Electron Microscope (SEM)

Secondary electron images were taken in Zeiss Merlin Gemini SEM system (Figure 2-11), a shared facility provided and maintained by MIT Materials Research Laboratory (MRL). The equipment is equipped with a sample load-lock chamber, which improves the sample
loading/unloading efficiency and minimizes the amount of contaminants getting into the main chamber. Spatial distribution of signal sources available in SEM is illustrated in Figure 2-12. To minimize the frequency of scattering event before arriving the substrate, the electron beam is operated in high vacuum (HV, $P_{\text{base}} < 5 \times 10^{-6}$ torr). During imaging, the electron beam energy is controlled at 1 keV, and the beam current is at 100 pA.

![Merlin SEM](image)

Figure 2-11 Zeiss Merlin scanning electron microscope, MRL, MIT. The control panel (right), is connected to the SEM (left).

The raster scan of the electron beam illuminates the sample with user-defined scanning area and scanning speed (or, dwell time). The escape depth of secondary electrons (SE) is in the order of a few nanometers, so the contrast of SE images is mostly from topography of the sample surface. The SE detector is an optoelectronic intensifier with positive bias to attract the SE from the sample surface. All of the SEM images used throughout this thesis were all collected in SE mode. Contrast of backscattered electrons (BSE), on the other hand, depends
strongly on the atomic weight of the sample. Therefore, the compositional contrast dominates in the BSE image.

Figure 2-12 Spatial distribution of signal sources available in SEM. PE: primary electron; SE: secondary electron; BSE: backscattered electrons; AE: Auger electrons and X: X-ray photons, CL: cathodoluminescence.  

2.2.5 Scanning Transmission Electron Microscopy, STEM

As an electron beam-based imaging technique, STEM enables atomic resolution characterization of thin samples in vacuum. A high-energy focused electron beam scans across the sample, generating signals of sample information, including the composition, crystal structure and electronic structure. Among these signals, high angle annular dark-field (HAADF) and energy dispersive X-ray spectroscopy (EDS) are used to analyze the TMD samples in the thesis.
HAADF imaging is realized by placing a ring-shaped detector with its center aligning the primary beam, as illustrated in Figure 2-13 (a). The detected electrons in HAADF mode are scattered at high angles, due to its Coulomb interaction with the nucleus of the sample atoms. The fraction of electrons scattered at high angles strongly correlates with the atomic number \( Z \) of the sample atoms, with heavier elements yielding stronger scattering than lighter elements. The intensity of a HAADF signal can therefore be used to provide Z-contrast information.

EDS is a composition characterization technique detecting the characteristic X-ray emitted from the sample due to the relaxation of electrons after the sample is illuminated by the primary electron beam. As depicted in Figure 2-13 (b), the incident electron knocks out the electron at the ground state of the inner shell, leaving an empty state there. The electrons at other outer shells could now relax to the empty state, after which the X-ray with corresponding photon energy is emitted. Combining STEM with EDS, the data could be...
collected in mapping mode, providing spatial distribution of material composition.

The theoretical resolution of STEM scales with the wave length, $\lambda_e$, of the incident electron beam, which can be described by Equation 2-3

$$\lambda_e = \frac{h}{\sqrt{2m_0E(1 + \frac{E}{2m_0c^2})}}$$  

where, $h$ is Planck’s constant, $m_0$ is the rest mass of an electron, and $E$ is the kinetic energy of the electron. The resolution of STEM imaging can therefore be improved if the beam energy is higher. However, compromise has to be made for STEM imaging of 2D TMD samples, which is sensitive to inelastic scatting events by incident electron beams. The momentum transfer from the incident electron to the sample could cause the ejection of sample atoms, especially when the TMD sample is atomically thin. As illustrated in Figure 2-14, the X atom is ejected from the monolayer MX$_2$ crystal illuminated by an electron beam, leaving a single X site vacancy, V$_X$. To avoid introducing defects during STEM imaging, the electron beam energy is generally controlled below 80 keV$^{26,73}$.

Figure 2-14 Stochastic X atom ejection event from the MX$_2$ sample in a stream of electrons. Blue balls: transition metal atoms; yellow balls: chalcogen atoms.
2.3 Substrate Engineering: Charged Beam Exposure

2.3.1 Mechanism of Sample Charging

During imaging using electron beams, sample charging could be a cause of image artifact, especially when the sample is not conductive. For example, if the sample is positively charged, then the secondary electrons created by the primary beam would be dragged by the electric field induced by the sample static charge. The secondary electron intensity is therefore locally suppressed.

One can calculate the amount of charge trapped in the sample based on charge conservation, as illustrated in Figure 2-15. Before exposure, the total charge of the whole system is just the charge of primary beam, \( Q_p \), assuming the initial charge in the sample is zero. After exposure, there are several components of charge in the system. First, back-scattered electrons (\( Q_{BSE} \)) and secondary electrons (\( Q_{SE} \)) are the charge escaping from the surface. Second, the electrons could penetrate the sample (\( Q_{out} \)) if the energy of the primary beam is sufficient. Finally, charge trapped in the sample (\( Q_{Sample} \)) to satisfy the charge conservation. One can write,

\[
Q_p = (Q_{BSE} + Q_{SE}) + Q_{out} + Q_{Sample}.
\]
Figure 2-15 Analysis of charging in dielectric sample exposed by an electron beam. Charge components of the whole system before (a) and after (b) exposure. $Q_P$, charge in primary beam; $Q_{SE}$, charge of secondary electrons. $Q_{BSE}$, charge of back scattered electrons. $Q_{Sample}$, charge trapped in the sample. $Q_{out}$: charge penetrating out of the sample.

We can then define total yield, $\sigma_t$, as the ratio of the charge collected from the sample surface to the charge of the primary beam,

$$\sigma_t = \frac{Q_{BSE} + Q_{SE}}{Q_P} \quad 2-4$$

The dependence of $\sigma_t$ on primary beam energy has been extensively studied. As depicted in Figure 2-16 (a), there are two cross-over energies, $E_1$ and $E_2$, where the yield is 1. If $E_1 < E < E_2$ and the sample is sufficiently thick so that primary electrons are all trapped in the sample (thickness $t >$ electron range $R$), then the sample is positively charged because more electrons escape from the sample than electrons trapped in the sample. If $E_2 < E < E_3$ ($t > R$), the sample is negatively charged. If $E > E_3$, then $Q_P = Q_{out}$. Therefore, the charge trapped in the sample, $Q_{Sample} = -(Q_{SE} + Q_{BSE})$, is positive. The consequent sample potential as a function of is shown in the plot of Figure 2-16 (b).
Figure 2-16 Dependence of total electron yield (a) and the sample potential (b) to the primary beam energy. (a) and (b) are adapted from Ref. 71.

2.3.2 Electron Beam Exposure: SEM

In addition to secondary electron imaging (discussed in Section 2.2.4), the electron beam in the SEM is also used for intentional electron exposure in my thesis. The electron dose is determined by multiplying the beam current (fixed at 100 pA in Zeiss Merlin SEM) and the exposure time, which can be controlled by choosing the scanning speed. The dose of electron beam exposure is the product of electron beam current and measured exposure time, divided by exposure area.

The side effect of electron beam exposure includes amorphous carbon deposition, if the equipment has been heavily used for various materials and/or the oil contamination from the mechanical pump is not controlled, trapped, or avoided. The amorphous carbon deposition is confirmed by characteristic D band and G band Raman modes, and the topography observed in AFM images. Experimental methods of Raman spectroscopy and AFM are introduced and discussed in Section 2.2.1 and Section 2.2.2, respectively.
2.3.3 Electron Beam Exposure: Electron Beam Lithography

The guided substrate engineering is realized by electron beam lithography (EBL) tools. With electromagnetics lenses connected to the beam controller, the electrons are directed and exposed on the sample with high repeatability and resolution. Electron beam with various beam parameters is exposed on thick silicon dioxide films (300 nm) and native oxide (2 nm), with the same p-type silicon substrate. To better navigate the sample after electron beam exposure, the substrate is mechanically scratched by a SiC scribe, making a $\sim$ 3 mm long scratch on the substrate. The optical images of the region of interest were then taken and stored for future navigation (Raman, AFM, SKPM, etc).

Raith 150 EBL system (Figure 2-17) provides beam energies from 0.2 to 30 keV. It comes with a 10 Mhz pattern generator with minimum dwell time increments of 2 ns. The Gemini column can achieve extremely small probe sizes at very low acceleration voltages. Its load-lock chamber significantly reduces the time needed for pump-down, and minimizes the contaminants from the ambient. The designed pattern files are generated by CleWin 5 software. Before each exposure experiment, the beam current is measured by placing the focused electron beam at the integrated Faraday cup. The measurement result is then fed back to the controlling software, which then automatically calculates the dwell time needed for electron dose given by the user. For our purpose in the thesis, there is only one pattern layer exposed on the blank substrate, so only course stage alignment was performed before the exposure sequence.
Figure 2-17 Raith 150 electron beam lithography tool, MTL, MIT. The sample is loaded in the chamber with electron gun and electron optics (the white box in the left), which are controlled by a computer with user interface (right) and digital design pattern files.

JEOL JBX-6300FS (Figure 2-18) is a high throughput system, running at 25 kV, 50 kV and 100 kV acceleration voltages. It has multi-cassette loader and is able to process samples with size up to 4-inch in diameter. Samples prepared in Figure 5-11 were exposed at 100 keV mode. The standard procedure of JBX-6300FS includes mandatory substrate alignment, which causes the workable sample area distant from the scratches made on the sample. The electron beam exposure when using JBX-6300FS was therefore switched to manual image mode, with the same procedure discussed in Section 2.3.2.
Figure 2-18 JEOL JBX-6300FS electron beam lithography tool, CA2DM, NUS. The sample is loaded in the chamber with electron gun and electron optics (right), which are controlled by a computer with user interface (left) and digital design pattern files.
Chapter 3 Guided MoS$_2$ Removal: Defect-mediated Nanopore Formation

This chapter is adapted from Ref.74 with permission of ACS Publications: Ke, J., Garaj, S., and Gradečak, S., Nanopores in 2D MoS$_2$: Defect-Mediated Formation and Density Modulation, ACS Applied Materials and Interfaces, 2019, 11, 26228

Abstract

Oxidation is a scalable process for introducing nanopores in two-dimensional transition metal dichalcogenides (TMDs) for membrane applications. The nanopore density formed by its oxidation is determined by the areal density of their nucleation sites; understanding the nature of the defects and their control would enable tailoring of TMD membranes for targeted applications. In this chapter, guided MoS$_2$ removal is realized by increasing the nanopore nucleation sites through intentionally introducing defects. We show that the nanopore distribution is dramatically different in strained and unstrained MoS$_2$ crystals. The location of underlying structural MoS$_2$ defects is revealed by unusual nanopore arrays observed in strained MoS$_2$ crystal, without requiring extensive atomic scale imaging across micron-scale. This spatial distribution is then correlated to the underlying arrangement of dislocations in MoS$_2$ crystals, in contrast to previously suggested sulfur vacancies.
3.1 Introduction

Two-dimensional (2D) materials including graphene and transitional metal dichalcogenides have attracted significant attention due to their extraordinary physical and chemical properties when a single layer is isolated from bulk. Physical and/or chemical properties of 2D materials can be further modified by engineering structural defects including point defects,75,76 grain boundaries77,78, and nanopores/voids17,37,38,79–83— an extreme case of a point defect cluster. Due to their sub-nanometer thickness, 2D materials decorated with nanopores are promising candidates for applications including DNA translocation37,79,80,84, water filtration/desalination81–83,85, energy harvesting38 (discussed in Section 1.2) or catalyst for hydrogen evolution reaction (HER)17,43,44 (discussed in Section 1.2).

To fully exploit the potential of 2D membranes and address the trade-off between their permeability and selectivity (more details in Section 1.2), the pore size and areal density have to be independently optimized and controlled. For example, nanopore density of ~10^{11} \text{ cm}^{-2} would be required for efficient reverse electrodialysis (RED)38 and HER devices17. It has been suggested that sulfur vacancies (V_{s}), the most abundant defect species in MoS_{2}, serve as the nucleation sites for the nanopore formation23. However, even though the reported areal density of sulfur vacancies [V_{s}] in MoS_{2} is ~10^{13} \text{ cm}^{-2} 86,87, the nanopore density formed by MoS_{2} oxidation is in the range of 10^{6} - 10^{9} \text{ cm}^{-2} 23,24,88, more than four orders of magnitude lower than [V_{s}]. As sulfur vacancies are observed to be uniformly distributed in MoS_{2}86, it is unlikely that vacancy clusters could explain the concentration mismatch, suggesting that other factors may be the major driver for the nanopore nucleation. Therefore, to bridge the gap between the oxidation-driven vs. targeted pore densities for more deterministic pore formation approach,
understanding of the underlying mechanism beyond nanopore formation is critical.

Motivated by bulk samples in which preferential etching has been traditionally used to form surface etch pits and study dislocation distribution\textsuperscript{42,89}, here we show that MoS\textsubscript{2} oxidation represents a two-dimensional analog of the same technique: nanopores formed in MoS\textsubscript{2} reveal the underlying structural defects at which preferential nanopore nucleation takes place. By investigating the spatial distribution and density of nanopores in strained and unstrained MoS\textsubscript{2} crystals, we directly correlate the material deformation with the spatial distribution of dislocations and nanopores in MoS\textsubscript{2}. We then provide a dislocation-based model, which governs nanopore nucleation during oxidative annealing in MoS\textsubscript{2}.

3.2 Scalable nanopore formation

The early work in the field of nanopores based on 2D materials has benefitted tremendously from an approach in which individual nanopores are formed in a 2D membrane using electron beam (e-beam) drilling inside a transmission electron microscope (TEM)\textsuperscript{37,79} (Figure 3-1). In this approach, 2D crystal is first transferred from the growth substrate to a supportive substrate, so that the crystal is partially free-standing, as depicted in Figure 3-1 (a). Prior to the transfer, the supporting substrate is prepared by focused ion beam to form holes with \( \mu \text{m} \)-level diameter over which the 2D crystal is overlaid making it susceptible to e-beam drilling. This approach has been the central to some of the proof-of-concept devices and has yielded interesting insights into single nanopore functionality, but it has limited scalability because it is serial in nature (and therefore relatively slow), expensive, and it requires precise
beam control in TEM. Another limitation of the approach is the sample size, which has to be compatible with TEM sample holder.

Alternatively, annealing in the oxidative environment\textsuperscript{23,24} is a scalable method for nanopore formation in transitional metal dichalcogenides (TMD) materials. In this technique, oxygen molecules react with 2D TMDs such that multiple nanopores nucleate and grow in parallel. The edges of nanopores formed by oxidation, as depicted in Figure 3-1 (b) and discussed in Section 1.1.1, are facets along ZZ direction. As the oxidation does not require expensive vacuum system, electron beam in TEM or special sample preparation, this approach has a potential for large-scale nanopore formation that is fast and cost-effective.

![Figure 3-1](image.png)

Figure 3-1 Nanopore formation processes for 2D membranes. (a) Nanopore formation by electron beam drilling in a TEM (left panel), and the representative TEM image of the resulting
nanopore (right panel). (b) Nanopore formation by oxidation in air (right panel), and the MoS$_2$ crystal model (left panel) of the nanopores after oxidation.

MoS$_2$ crystals used in this chapter were prepared by CVD process developed in our laboratory. The CVD procedure is described in Section 2.1.2, including substrate preparation, temperature control, precursors chosen, carrier gas choice, and the gas flow rate. For the oxidative annealing process conducted in this thesis, as-prepared MoS$_2$ samples were placed on a hotplate in a fume hood. The hotplate was preheated to the target temperature and standby for 10 min before annealing. After annealing, the samples were removed from the hotplate and were put on a piece of aluminum foil to cool down. The oxygen reacts with MoS$_2$ and a volatile product MoO$_2$(OH)$_2$ is formed, which leaves the sample surface and forms triangular pores with zigzag edges in the MoS$_2$ crystal, as shown in the atomic model of Figure 3-1 (b). More discussions about MoS$_2$ crystal shape and nanopore edge orientation are included in Section 1.1.1.

Similar to all other chemical reactions in general, the activation energy associated to nanopore formation process by oxidation can be engineered to control the rate of reaction. The strategy of guided MoS$_2$ removal in this chapter (and in Chapter 4 as well) is therefore increasing the nanopore nucleation sites by intentionally introducing defects in MoS$_2$ crystals. In addition to controlling nanopore density, the observed nanopore distribution in MoS$_2$ could potentially provide indirect material information.
3.3 Guided MoS$_2$ removal by strain effect

Defect engineering in MoS$_2$ is realized by introducing deformation, followed by oxidation process to form nanopores. Unstrained and strained MoS$_2$ samples were prepared by chemical vapor deposition (CVD, details provided in Section 2.1.2) using different cooling rates. MoS$_2$ crystals prepared using slow cooling rate (4°C/min) shown in Figure 3-2 (a) have equilateral triangular shapes (all angles are $\approx 60^\circ$), which indicates no apparent macroscopic deformation. In distinct contrast, significant deformation can be observed in MoS$_2$ crystals that experienced faster cooling rate (80°C/min): the crystal edges appear concave with the corner angles significantly <60° (Figure 3-2 (f)). In addition to the difference in the overall crystal shape, the nanopore distribution in the correspondingly annealed samples shows a dramatic difference. Figure 3-2 (c) and (d) show representative SEM images of unstrained and strained MoS$_2$ crystals, respectively, after annealing in air at 300 °C for 15 min. In unstrained MoS$_2$ the nanopores are distributed randomly (Figure 3-2 (d)), whereas nanopores in the strained crystals are distributed along preferred orientations (Figure 3-2 (d) and Figure 3-3).

As the nanopore distribution depends strongly on the cooling rate, which in turn dictates the strain level and defect distribution in the resulting crystals, we further investigated the pore formation in exfoliated MoS$_2$ crystals, which are considered to be strain-free\textsuperscript{91}. These samples exhibit randomly distributed nanopores (Figure 3-2 (e)), further corroborating the strong relationship between material deformation and the underlying defect species that act as nucleation sites for nanopores in MoS$_2$. Taken together, our results indicate that the pore nucleation mechanism could be related to defect species other than sulfur vacancies.
Figure 3-2 Correlation between MoS$_2$ deformation and nanopore distribution. (a) and (b) Representative dark-field optical images of triangular (grown at lower cooling rate) and concave triangle (grown at higher cooling rate) CVD-MoS$_2$ crystals, respectively. Dashed lines in (a) and (b) show an outline of equilateral triangles. (c) and (d) Representative SEM images of the nanopore corners in triangular and concave triangle CVD-MoS$_2$ crystal, respectively. (e) SEM image of nanopores in exfoliated MoS$_2$. (f) The measured corner angle in (b) is 49.4°. Images in (c)-(e) were taken after annealing at 300°C for 15 min. Arrows in (d) indicate two of the nanopore arrays in the strained MoS$_2$ crystal.

Figure 3-3 Low-magnification SEM images of strained MoS$_2$ crystals. Yellow dashed box in
where $C_1$ and $C_2$ are positive constants; $x$ and $y$ are coordinates relative to the origin defined at the dislocation at the center. The $y$-component (second term) is in the climbing direction, which we can ignore in the discussion here because dislocation climbing is governed by vacancy diffusion, not by the force exerted on the dislocation. The $x$-$y$ space can therefore be split into attractive (shaded area in green) and repulsive (area in white) domains based on the sign of $x$-component of the force. Final dislocation distribution can be predicted by simulation based on Peach – Koehler force discussed above\(^3\). As shown in Figure 3-4 (b)\(^3\), the dislocations rearrange to release strain energy by forming arrays.

To minimize the total strain energy, the dislocations tend to form arrays along the climbing direction by gliding. The behavior has been confirmed by experimental results, in
which the dislocations were revealed by preferential etching starting at dislocation cores. As a representative example, optical image in Figure 3-4 (c) depicts the dislocation arrays revealed by the etched pits on the gold surface\textsuperscript{94}. The concept has been widely used to evaluate the dislocation densities in LiF\textsuperscript{42}, silver\textsuperscript{95} and gold\textsuperscript{94} crystals. MoS\textsubscript{2} oxidation, as a form of etching, is an ideal method to probe the underlying structural defects.

Figure 3-4 Dislocation-dislocation interaction and resulting distribution. (a) Attractive (shaded area in green) and repulsive (area in white) domains due to the strain field built by the dislocation at the center. The arrows indicate the corresponding force direction. (b) Dislocation array formation after strain energy minimization. (c) Optical image of etched gold surface revealing the dislocation distribution. (b) and (c) are adapted from Ref.93\textsuperscript{93} and Ref.94\textsuperscript{94}, respectively.

Here, we use a two-dimensional analogy of dislocation arrays to the ones found in a bulk crystal\textsuperscript{94} and show they are self-consistent with the unique nanopore distribution observed in Figure 3-2 (d). The atomic structure of two 5|7 dislocations in 2D MoS\textsubscript{2} is depicted in the right panel of Figure 3-5 (a). The Burgers vector, \textbf{b}, of a 5|7 dislocation is along ZZ direction and its climbing direction is along AC, perpendicular to \textbf{b} (refer to Figure 1.5 for detailed atomic structure), same as the direction of nanopore arrays in the strained samples (Figure 3-2 (d) and
Figure 3-5 (b)). Importantly, the climbing direction and the Burgers vector of other dislocations in 2D MoS$_2$ (such as 6|8 or 4|6) are the same as for 5|7 dislocations, even though the atomic structures of these dislocations vary at the dislocation cores$^{26,27,96}$.

Figure 3-5 Mechanism of MoS$_2$ nanopore array formation. (a) Atomic model of an MoS$_2$ crystal with S-ZZ edges (blue lines), a simple pore array along the AC direction (left) and two 5|7 dislocations aligning along AC direction (center). Atoms on AC and ZZ edges are labeled in green and in blue, respectively. (b) Higher magnification image taken from Figure 3-2 (d) to illustrate the pore array geometry relatively to the crystal facet.

The proposed model for nanopore array formation in MoS$_2$ is illustrated in Figure 3-6 and is based on the array geometry shown in Figure 3-2 (d) and Figure 3-3. During the cooling phase of the growth, dislocations are introduced due to the thermal expansion coefficient mismatch between MoS$_2$ (7.6$\times$10$^{-6}$ °C$^{-1}$)$^{97}$ and Si/SiO$_2$ (0.24$\times$10$^{-6}$ °C$^{-1}$)$^{98}$ substrate. The MoS$_2$ crystal grown at high temperature therefore has to shrink more than SiO$_2$ does to release thermal strain energy. To further minimize the total strain energy, mobile dislocations redistribute and form arrays along their climbing direction due to mutually attractive and repulsive forces$^{92,99}$, as we discussed in Figure 3-4 (a). As a result, dislocations in MoS$_2$ form arrays along climbing direction (i.e. AC, as shown in Figure 3-5 (a)).
Figure 3-6 Schematic illustration of the proposed nanopore array formation mechanism: random distribution of dislocations (bottom left), dislocation arrays form (middle), and nanopore formation (bottom right). The nanopore arrays reveal the distribution of dislocations, which redistributed in strain fields.

The observed dislocation arrays can be described as ultralow angle grain boundaries, each corresponding to a small misorientation of 0.1°—0.4°. For small-angle tilt boundaries, as illustrated in Figure 3-7 (a), the misorientation \( \theta \) between two crystal domains can be expressed by Equation 3-2 with measured average distance \( d \) between neighboring dislocations and known Burgers vector magnitude \( b^{100} \):

\[
\theta = \frac{b}{d}
\]

3-2

In our case, we first assume that at the center of each nanopores in the nanopore array, there was originally a dislocation core serving as a nucleation site. We can then use the dislocation
array structure depicted in Figure 3-7 (b) to estimate $\theta$ by applying the measured nanopore spacing within an array as $d$ in Equation 3-2.

As an example, the angle measured from a MoS$_2$ crystal corner in Figure 3-7 (c) is 48°. Each $d = (45–150)$ nm was measured from the distance between neighboring nanopores in an array, as shown in Figure 3-7 (d), and known $b = 0.315$ nm was used to calculate the corresponding angle $\theta_0$ (Equation 3-2). As a result, each dislocation array corresponds to a small misorientation $\theta_0 = 0.1°–0.4°$. Finally, cumulatively, a set of semi-parallel tilt boundary dislocations observed in strained MoS$_2$ samples add up to the finite concave facet with total misorientation $\theta_{total}$, by multiplying total number of pore arrays on semi-edges, $N$, by the misorientation $\theta_0$ per array.

$$\theta_{total} = N\theta_0$$  \hspace{1cm} 3-3

Equation 3-3 yields $\theta_{total} = 7.8°–31.2°$, and the measured angle offset, 12°, is within the calculated range. The overestimation of the rough approximation above could be explained by the factors discussed below. First, we assumed that all of the pores in the pore array nucleated at a dislocation core, but complex defect species other than dislocation (see Section 1.1.2) could also play a role in nanopore nucleation, as we will discuss further in Section 3.4. Another factor is the sign of the dislocations. As depicted in Figure 3-7 (b), we have assumed that all dislocations are of the same sign, but there are dislocations with both signs, whose contribution of MoS$_2$ crystal deformation cancel each other. The dislocations with the opposite sign could be randomly distributed in the crystal, or, they could form dislocation array based on the same mechanism we have discussed in Figure 3-6.
Because of higher local lattice distortion near dislocation cores compared to sulfur vacancies and other defect species, we can expect lower activation energy for nanopore nucleation at these sites. As a result, both the spatial distribution of the nanopore arrays and the resulting macroscopic deformation of the strained crystals are consistent with the pore nucleation at the dislocation cores.

Figure 3-7 (a) Low-angle grain boundary structure in simple cubic crystals. “⊥” labels the dislocation core locations. (b) Ultralow grain boundary structure of MoS$_2$. The color code follows the one used in Figure 3-5 (a). (c) High magnification SEM image of Figure 3-3 (b). (d) High-mag SEM image taken from the area in (c). Arrows indicate the pore location. (e) Total number of pore arrays on semi-edges of the same corner in (c). Figure in (a) is adapted from Ref. 100.
3.4 Majority and minority defects in MoS$_2$

We further suggest that nucleation sites for the randomly scattered nanopores (the ones that are not found in more ordered arrays) can be attributed to other minority defect species in MoS$_2$, including complex point defect clusters and dislocations and that the pore nucleation probability is related to their corresponding strain energies. Relative population of defect species in MoS$_2$ is qualitatively illustrated in Figure 3-8 based on previously reported data$^{86,87}$. In CVD-grown and mechanical exfoliated MoS$_2$, density of sulfur vacancies is at least an order of magnitude higher than the density of all other defect species (collectively referred as minority defects). As mentioned above, individual sulfur vacancies are unlikely nanopore nucleation sites, which could be ascribed to small strain fields (deviation from the perfect crystal structure) associated with these defects, also supported by its low formation enthalpy$^{86,101}$. Therefore, other minority defects associated with larger strain fields should be energetically more favorable for nanopore nucleation and randomly distributed nanopores observed in Figure 3-2 (c) and (d) reveal the location of randomly distributed dislocations and/or other defect species (MoS$_2$ and V$_{MoS6}$, etc.).

![Figure 3-8 Relative population of majority (V$_S$, sulfur vacancy, left panel) and minority (right panel) defect species in CVD-grown MoS$_2$. V$_{S2}$: disulfur vacancy; V$_{Mo}$: molybdenum vacancy; V$_{2S2}$: double disulfur vacancy; D: dislocation; Mo$_S$: substitutional molybdenum on two sulfur](image-url)
sites; Mo$_5$: substitutional molybdenum on a sulfur site. All defect population data except dislocation density is extracted from Ref. 86. Dislocation density is approximated to illustrate its relative population.

The pores observed in CVD-MoS$_2$ crystals grown using slower cooling rate are significantly larger (80 – 220 nm) than the ones grown using faster cooling rate (≤ 30 nm), as shown in Figure 3-2 (c) and (d). This difference in the nanopore growth rates is likely associated with different concentrations of majority defects (e.g. sulfur vacancies) in the starting MoS$_2$ crystals grown at different cooling rates. Although we show that the majority defects are not responsible for the nanopore nucleation, they lower the oxidation activation energy and thus increase the nanopore growth rate. To control the desired pore size independently with fixed pore density, annealing duration time could be determined based on the growth rate calibration. As shown in the MoS$_2$ SEM images in Figure 3-9, the pore size increased when the annealing duration was extended, whereas no extra pore nucleation was observed. Nanopore formation behavior reported in Ref.102 agrees well with the phenomenon observed in Figure 3-7, which indicates that the minority defects were consumed by nanopore nucleation at the early stage of MoS$_2$ annealing, and the annealing temperature is not sufficient to overcome the activation energy of nanopore nucleation at majority defects (sulfur vacancies).
3.5 Conclusion

In this chapter, we have investigated the oxidative nanopore formation in CVD-MoS\(_2\) crystals annealed in air. Based on the experimental results, we then proposed a nanopore nucleation model in which the minority defects (defect species other than V\(_s\)) in MoS\(_2\) are likely to govern the pore nucleation process. Specifically, the spatial arrangement of the nanopores in highly strained MoS\(_2\) crystals and the resulting crystal deformation is self-consistent with the model of dislocation arrays as the nanopore nucleation sites. The macroscopic deformation of MoS\(_2\) is attributed to the accumulation of microscopic deformation of dislocations forming arrays, which are revealed by nanopore formation in MoS\(_2\). Estimation of the MoS\(_2\) deformation by nanopore array number and the pore spacing agrees with the measured macroscopic deformation. Alternatively, based on our results in this chapter, the oxidative annealing process can be used as a defects diagnostics tool for rapid materials control.
Chapter 4 Guided TMD Removal: Electron Beam and Laser Beam Effects

Abstract
Oxidation is a scalable process for introducing nanopores in 2D TMDs for membrane applications. The nanopore density formed by its oxidation is determined by the areal density of their nucleation sites. Therefore, development of the defect engineering in TMDs would enable tailoring of TMD membranes for targeted applications. In this chapter, to control the nucleation density of MoS$_2$ nanopores, we demonstrate that the pore density can be modulated by electron beam exposure prior to the oxidative nanopore formation. Raman analysis of electron beam-exposed samples indicates that hydrocarbon adsorption activates defect species other than dislocations, which significantly enhances the nanopore density in MoS$_2$. Laser beam exposure, another beam-based treatment, is also proven to locally enhance the etching of mechanically exfoliated WS$_2$ under regular wet transferring protocol.
4.1 Introduction

As introduced in Chapter 1, both membrane applications such as RED and catalysis applications such as HER require controllability of higher areal nanopore density, which improves the current density for RED devices and increases the catalysis efficiency of HER devices. The observed nanopore density of pristine CVD-MoS$_2$ after annealing in air (e.g. $2.2 \times 10^9$ cm$^{-2}$ in Figure 3-2 (c)) is lower than the targeted densities ($\sim 10^{11}$ cm$^{-2}$) for membrane and catalysis applications. Boosting nanopore density is therefore needed to improve the RED current density and increase the catalysis efficiency of HER devices. In Chapter 3, we have demonstrated that it could be realized by introducing macroscopic deformation.

Although strain engineering described in Chapter 3 provides a mechanism of modifying the pore density, as evidenced by increased nanopore density in strained MoS$_2$ crystals ($\sim 10^{10}$ cm$^{-2}$ in Figure 3-2 (d)), this process is less controllable for practical applications. In particular, when the nanopores are not distributed randomly (e.g. when the nanopores form arrays), the ones located in the area with higher pore nucleation density are more likely to merge, forming larger pores if the inter-pore distance is smaller than the pore diameter. This effect could be detrimental to RED devices, because the nanopore diameter is no longer optimized for best ion selectivity resulting in the reduced RED power efficiency. Merged nanopores could also impact mechanical strength of the 2D membrane, which has to withstand the osmotic pressure between the neighboring cells, as shown in Figure 1-7. The catalysis efficiency of HER material would also be impacted, because the catalytic active sites vanish when the nanopores merge. Therefore, an extrinsic technique to control density and location of nanopore nucleation sites would be required to suppress the nanopore merging process.
To approach the aforementioned goal of guided TMD removal, effect of electron beam and laser beam exposure on MoS$_2$ and WS$_2$ are studied in this chapter. Both of these beam-based techniques provide customizable pattern design by a user, which is essential to complex device design. After the beam treatments, extrinsic structural defects are introduced. In this chapter, we show that the activation energy required for pore nucleation can be lowered using electron beam exposure, which can be controlled to engineer the pore density, particularly in the high-density regime required for membrane applications. We then demonstrate that defects and nanopores are introduced by laser exposure on exfoliated WS$_2$ crystals. The preferential WS$_2$ removal demonstrated in this chapter provides an alternative to TMD treatment for guided material removal, despite its rudimentary patterning resolution.

4.2 Guided nanopore formation by electron beam exposure

Results in this section are adapted from Ref. 74 with permission of ACS Publications: Ke, J., Garaj, S., and Gradečak, S., Nanopores in 2D MoS$_2$: Defect-Mediated Formation and Density Modulation, ACS Applied Materials and Interfaces, 2019, 11, 26228

Based on the findings in Chapter 3, we next consider methods that either modify the number of intrinsic defects that are responsible for the pore nucleation and/or affect annealing temperature required for their activation. We demonstrate that the nanopore nucleation in CVD-MoS$_2$ can be modulated by irradiating the material with an electron beam and that the beam dose enables the pore density control.
The procedure of guided nanopore formation is illustrated in Figure 4-1. As-grown CVD-MoS$_2$ samples were first exposed by an electron beam in a scanning electron microscope (SEM), followed by the identical oxidative annealing process described in Section 3.2 to form nanopores. During electron exposure, the SEM is operated in imaging mode (details see Section 2.2.4) with much slower scanning speed (~1.4 min per frame). The electron dose, $D_e$, is calculated by the Equation 4-1,

$$D_e = \frac{I_{beam}\Delta t}{eA}  \quad 4-1$$

where $I_{beam}$ is beam current; $\Delta t$ is total exposure time; $e$ is unit charge; $A$ is exposure area.

As shown in the SEM image of Figure 4-1, the nanopore density can be qualitatively compared between each area. The light-grey matrix in the SEM image is MoS$_2$, whereas the dark-grey triangles are nanopores, with the edges following the preferred ZZ crystal orientation. In the low electron dose area next to the scale bar, the nanopore density is significantly higher than the pristine area. Furthermore, area irradiated by higher electron dose per area shows higher pore density. In both of the e-beam exposed areas of Figure 4-1, the average inter-pore distance is comparable to or less than the nanopore size, which makes it difficult to quantify the areal nanopore density.
Figure 4-1 Schematic illustration of the electron beam exposure of a MoS$_2$ crystal followed by the oxidative nanopore formation and a representative SEM image of the resulting crystal. Nanopore density is significantly higher in the area irradiated with an electron beam (outlined by dashed lines), and the density can be controlled by the electron beam dose.

To quantify the effect of e-beam exposure on nanopore density, CVD-MoS$_2$ crystals were exposed by two electron beam doses with the same electron energy (1 keV). We intentionally focus on two neighboring grains to demonstrate that electron-beam induced effects are not site- or grain-specific. The lower part of Figure 4-2 (a) was irradiated once by an electron beam (labeled as low dose), whereas the upper part was exposed twice by the same electron dose (labeled as high dose). After the e-beam exposure and subsequent annealing at 300°C for 15 min, the nanopore density was measured from the SEM image shown in Figure 4-2 (b). Two distinct grains (labeled as 1 and 2) can be observed, as evidenced by preferential decomposition at the grain boundary and the orientation of triangular nanopores in each grain. The exposed area in Figure 4-2 (c) crosses a grain boundary so that nanopore densities can be measured and compared between neighboring grains processed with the same conditions, including electron beam exposure, CVD growth and oxidative annealing.
Nanopore density as a function of the electron beam exposure is summarized in Figure 4-2 (c). As in the cases discussed above, the nanopore density in as-grown, non-irradiated CVD MoS$_2$ is $\sim 10^9$ cm$^{-2}$. As the dose of e-beam exposure increases, up to ~30-fold increase in the nanopore density was observed in both grains for $8.0 \times 10^{17}$ electrons/cm$^2$ electron beam exposure prior to the nanopore formation via annealing.

Figure 4-2 (a) SEM image after electron beam exposure, but before nanopore formation. The doses used in the low and high dose areas are $4 \times 10^{17}$ cm$^2$ and $8 \times 10^{17}$ cm$^2$, respectively; (b) SEM image of the same sample region after annealing at 300 $^\circ$C for 15 min and (c) the corresponding nanopore densities measured at areas with different electron doses.

The observed nanopore density enhancement in Figure 4-2 (b) indicates that the activation energy and the corresponding threshold temperature required for the nanopore
nucleation decrease after e-beam exposure. We now consider effects of the electron beam that may be responsible for this density increase. Temperature rise caused by an electron beam is approximated by Equation 4-2.21:

\[
T = \frac{3IV_0}{2\pi \lambda R}
\]

where \( I \) is the beam current, \( V_0 \) is beam voltage, \( \lambda \) thermal conductivity of the sample and \( R \) is electron range. For a Si/SiO\(_2\) substrate, an electron beam with 1 keV energy yields \( R = 60 \text{ nm} \), and 100 pA therefore results in 0.8 °C increase in temperature. Because specimen heating induced by the electron beam is negligible, no heat-induced defect generation is expected. Furthermore, the electron beam energy (1 keV) used to irradiate the samples is well below the knock-out threshold energy (80 keV for MoS\(_2\)) by momentum transfer. Other defect species such as V\(_{\text{Mo}}\), S\(_{\text{Mo}}\), and dislocations are even less likely to be formed by momentum transfer because the associated formation energies are higher. Therefore, other mechanisms must be at play.

Figure 4-3 Defect introduction in MoS\(_2\) by electron beam exposure. (a) SEM image of the
exposed regions on MoS$_2$ crystals. (b) representative Raman spectrum from CVD-MoS$_2$
crystals with 633 nm laser. (c) $I_{LA}/I_E$ intensity ratio measured from e-beam exposed CVD-
MoS$_2$ at various dosage (left), and corresponding optical image. E-beam dosage for orange
and red data points in (c) are the same as “low dose” and “high dose” in Figure 4-2 respectively.

Figure 4-3 (a) shows a typical SEM image of a MoS$_2$ sample after electron beam
exposure. The dark contrast of exposed region in Figure 4-3 (a) can be assigned to the
unavoidable contamination in the SEM column$^{103,104}$; during the e-beam exposure,
hydrocarbon molecules in the SEM column are broken down to free radicals and deposited
onto the sample. Indeed, hydrocarbon deposition is observed in the atomic force microscopy
(AFM) image and the Raman spectrum (Figure 4-4) from the e-beam scanned MoS$_2$ crystal.

To further investigate the role of this process onto the underlying MoS$_2$ sample, exposed CVD-
MoS$_2$ samples were characterized using Raman spectroscopy. A typical Raman spectrum of
CVD-MoS$_2$ is shown in Figure 4-3 (b). LA(M) mode at 226 cm$^{-1}$ is associated with defects in
MoS$_2$ and the ratio of Raman intensities of LA(M) mode and E mode ($I_{LA}/I_E$) has been used
as a measure of the defect concentration in TMDs $^{63-66}$. $I_{LA}/I_E$ intensity ratio measured from
four areas of the same MoS$_2$ crystal exposed by different electron doses (Figure 4-3 (b)) show
that the $I_{LA}/I_E$ ratio of MoS$_2$ initially increases under the electron beam exposure up to a dose
of $4 \times 10^{17}$ cm$^{-2}$ and then flattens out with higher doses. This result indicates that the presence
of hydrocarbons modifies the nature of the existing defects or it catalyzes formation of defects
like V$_{MoS3}$ $^{27}$. Defect species originally inactive for pore nucleation become activated, as their
activation energy is reduced by the electron beam exposure. As a result, the nanopore density
is locally enhanced in regions exposed by electron beam. We note that although here we use
an electron-beam to modify the nanopore density, other treatments by charged particles $^{63,105-}$
$^{107}$ could be used to achieve similar effects.
Figure 4-4 Amorphous carbon deposition induced by electron beam exposure in a SEM. (a) Atomic force microscopy image collected from the area in Figure 4-3 showing thickness increase in the electron beam irradiated region of the sample. (b) Raman spectroscopy of these deposits showing carbon D and G bands, thus confirming hydrocarbon deposition during the electron beam scanning process.

4.3 Defect engineering of exfoliated WS_2 crystals by laser exposure

Results in this section were cooperative work with Kevin Bogaert. The figures used in section 4.2 are adapted in part from Chapter 5 of Kevin’s thesis^62.

Motivated by the work using electron beams in Section 4.2, now we consider other forms of irradiation that may be more susceptible to large-scale implementation. By well-designed optical components in laser optics, the laser system providing mm-scale exposure area with uniform intensity is available^108. Furthermore, the pore edges could serve as nucleation sites for TMD heterostructures preparation (Section 5.2). In this section, guided defect engineering in mechanically exfoliated WS_2 (ex-WS_2) crystal is realized by laser exposure. The process is illustrated in Figure 4-5. First, the initial crystal is prepared by mechanical exfoliation (Figure
Next, as shown in Figure 4-5 (c), the ex-WS$_2$ crystal is selectively exposed by choosing desired area, laser power, laser wavelength and exposure time in the mapping mode of LabSpec 6 software. Finally, as we will discuss in the next chapter, the sample is directly used as a growth template for CVD-MoS$_2$ process described in Section 2.1.2, and the preferential MoS$_2$ deposition is observed in the area with laser exposure, as depicted in Figure 4-5 (e).

Figure 4-5 Schematic (a)(c)(e) and optical images (b)(d)(f) of proof-of-concept guided MoS$_2$ deposition by laser direct-write exposure on exfoliated WS$_2$. (b)(d)(f) share the same scale bar.
The effect of laser wavelength on preferential MoS\textsubscript{2} growth is investigated. The three lasers with \textasciitilde10 mW power and exposure time were exposed on the same ex-WS\textsubscript{2} crystal, which is then characterized by Raman/PL and AFM. We have discovered that the laser exposure with photon energy (785 nm laser) lower than WS\textsubscript{2} optical band gap has virtually no effect on AFM, Raman/PL intensity\textsuperscript{62}, while both 532 nm laser and 633 nm laser exposure impact Raman/PL intensity.

To analyze the effects of laser exposure on the crystal, STEM imaging is used to image an ex-WS\textsubscript{2} crystal annealed with the 633 nm laser, as shown in Figure 4-6 (a) and (b). The circles in the image are holes of the holey grid, and the dark, grey band is the area with laser exposure. During the exposure, the laser was operated at line scan mode, which implies that it is the finest exposure feature available in the Raman equipment. Based on the STEM images and the EDS mapping images (Figure 4-6 (c)(d)), WS\textsubscript{2} is completely removed from the sample at the area with laser exposure. This could be due to the harsh sample treatments during sample transfer from SiO\textsubscript{2} substrate to the Cu TEM grid. Treatments including acetone and KOH attack the exposed area of ex-WS\textsubscript{2} much faster, revealing that the area became more defective after laser annealing.
Figure 4-6 (a), (b) HAADF STEM images of 633 nm laser exposed WS$_2$. EDS mapping of (c) W and (d) S collected from the same area shown in (b).

The phenomena observed in Figure 4-6 indicates that the laser annealing introduces structural defects in ex-WS$_2$, enhancing the WS$_2$ removal locally. The resolution (feature width measured in (a) = 1.3 µm) of this technique, however, is limited to the laser beam width (~1.5 µm). Therefore, the approach can be useful in the applications that require high throughput, large area treatment, but do not demand high spatial resolution. To demonstrate the concept, guided lateral heterostructure formation by laser treatment will be discussed in Chapter 5.
4.4 Conclusion

In this chapter, we demonstrate that material modification through defect engineering prior to nanopore formation is a promising direction for the nanopore density control for future 2D membrane applications. To modulate the nanopore density formed in MoS$_2$, one can use electron beam exposure to locally introduce defects, which promotes MoS$_2$ oxidation, forming denser nanopores. Alternatively, the preferential removal of WS$_2$ is observed after 633 nm laser exposure followed by wet transferring protocol. The concepts discovered in this chapter could potentially be applied for guided material removal in other materials systems by using guided beam material treatment.
Chapter 5  Guided MoS$_2$ Growth Processes

Abstract

Future implementation of two-dimensional (2D) materials for electrical and optical applications will rely on the ability to pattern these materials with high spatial resolution. Conventional patterning methods require polymer-based resists, which in the case of 2D materials is difficult to be removed completely and is often detrimental to the device performance. In this chapter, two resistless, bottom-up techniques of guided MoS$_2$ deposition are presented. First, MoS$_2$-WS$_2$ heterostructure is prepared by preferential MoS$_2$ growth on laser-exposed lines of exfoliated WS$_2$. We then demonstrate that MoS$_2$ can be preferentially deposited on areas of SiO$_2$ substrates that are exposed by the electron beam. We have explored the dependence of MoS$_2$ patterning quality on electron beam parameters, along with the mechanism of guided MoS$_2$ growth: charging in the substrate. We show that MoS$_2$ pattern resolution using our experimental setup is limited by MoS$_2$ grain size. Finally, based on scanning Kelvin probe microscopy, we have confirmed that positive charge is trapped in 300 nm SiO$_2$ after electron beam exposure. The guided MoS$_2$ deposition techniques presented in this chapter are potentially applicable for other 2D materials and beyond, simplifying the patterning process flow significantly.
5.1 Introduction

For decades, lithography has been the cornerstone of functional device technology advancement, especially the devices for integrated circuits. Being able to customize the material shape by patterning, one can design functional devices in a larger, integrated scale. Two-dimensional (2D) materials such as graphene\cite{1} and transition metal dichalcogenides\cite{2,5,109} (TMDs) exhibit many interesting properties that make them promising materials for novel electronic and optical applications\cite{110,111}. The fabrication of 2D electronic and optoelectronic devices requires patterning processes to define the desired circuits. Conventional top-down patterning methods\cite{112,113} rely on coating a polymer-based resist that is then exposed by photons or electron beams and developed by dedicated chemicals for the specific resist. After the subsequent selective etching of materials, the protective resist has to be removed.

Each of these steps adds to the process complexity, and in the case of 2D materials, potential materials damage\cite{47,48}. Furthermore, residual resist is detrimental to 2D devices, which is the reason why several attempts of cleaning the surfaces of 2D materials have been reported\cite{47–49}. To address the aforementioned issue, several bottom-up approaches have been suggested. For example, by depositing seeding precursor\cite{114} or periodic metal dots\cite{115,116} on the substrate, nucleation of 2D materials can be controlled at pre-designed locations. Another approach is to use plasma treatment\cite{117–119} with a pre-patterned mask protecting the substrate to selectively modulate the substrate surface energy, which enables locally enhanced material nucleation on the patterns.

These bottom-up approaches, however, still rely on substrate surfaces protected by
resists/masks, because the engineering treatments act universally on the substrate. Therefore, it is desirable to develop a guided substrate treatment technique, which modifies solely the designed area of the sample. Charged particle beams, including electron and ion beams, can be directed by computer-controlled electromagnetic lenses, realizing the selective substrate engineering without introducing resist/mask to protect the substrate. Hence, a resistless patterning method, by which materials are grown without any use of resist or mask, possesses great advantages over existing top-down and bottom-up alternatives.

In this chapter, guided MoS$_2$ deposition by selective substrate treatment is demonstrated. To realize this concept, laser exposure is applied to mechanically exfoliated WS$_2$ crystals (Section 5.2). To improve the selectivity of guided MoS$_2$ deposition, electrostatically-guided chemical vapor deposited (CVD) processes by electron beam exposure of the growth substrate in scanning electron microscope (SEM) is then demonstrated and discussed in Section 5.2. Customizable pattern growth with higher spatial resolution is then demonstrated by utilizing electron beam lithography (EBL) tool in Section 5.4. By locally embedding static charges in the thick SiO$_2$ layer, we demonstrate a resist-free patterning technique of CVD-MoS$_2$ process, in which MoS$_2$ growth is guided by direct electron beam exposure on SiO$_2$ substrates.
5.2 Guided MoS$_2$ deposition on exfoliated WS$_2$ crystals

Results in Section 5.2 were cooperative work with Kevin Bogaert. The figure used in Section 5.2 are adapted from Chapter 5 of Kevin’s thesis$^{62}$. As we have demonstrated in Chapter 4, laser irradiation efficiently introduces defects in ex-WS$_2$ crystals. Based on this approach, we now use laser irradiated ex-WS$_2$ as a template for MoS$_2$ growth, as illustrated in Figure 4-5 (e). To evaluate the resolution and the growth selectivity of CVD-MoS$_2$ on laser exposed ex-WS$_2$, Raman mapping technique was used to characterize the final heterostructure crystal. Two lines of contrast were observed in the optical ex-WS$_2$ crystal images of before and after laser exposure in Figure 5-1 (a) and (b), which indicates partial WS$_2$ removal by laser exposure. The guided MoS$_2$ growth on WS$_2$ by 532 nm and 633 nm laser is then confirmed by both the optical image and Raman E mode intensity mappings (Figure 5-1 (c)-(f)): MoS$_2$ crystals preferentially nucleate at the lines exposed by 633 nm and 532 nm laser. Raman intensity mapping shown in Figure 5-1 (f) indicates that 633 nm laser is more efficient on guided MoS$_2$ deposition, which could be explained by higher absorption of 633 nm photon by monolayer WS$_2$. Localized heating and partial decomposition of WS$_2$ are confirmed by SEM images after 633 nm and 532 nm laser exposure$^{62}$. The defects/pores induced by laser exposure on WS$_2$ crystal provide preferential MoS$_2$ nucleation sites, at which the activation energy is lower than the surrounding area. However, based on the Raman spectra shown in Figure 5-1 (g), the selectivity of is not ideal, which means that there is still some observable amount of MoS$_2$ (see Figure 5-1 (f) and cyan curve in Figure 5-1 (g)) outside of the laser-exposed area. The ideal patterning selectivity is the patterning technique such that the material deposits only on the designed area, whereas the technique with no selectivity yields pure random material deposition. In addition, the patterning resolution (the
MoS$_2$ line width) is limited by the laser beam size, which is about 1.5 µm in our experimental setup.

Figure 5-1 Optical images and Raman mapping images of guided MoS$_2$ deposition on an ex-WS$_2$ crystal. (a)-(c) Optical images of each stage of the guided deposition process. (d), (e) MoS$_2$ and WS$_2$ E mode Raman intensity mapping taken from (c), respectively. (f) Composite intensity image of (d) and (e), with the signal from MoS$_2$ in red and the signal from WS$_2$ in cyan. (g) Representative Raman spectra collected from the red area and the cyan area in (f). Scale bars are 5 µm. The scale bar in (a) applies to (a)-(c), and the one in (d) applies to (d)-(f).
5.3 Guided MoS$_2$ deposition on SEM exposed SiO$_2$ substrate

In Section 5.2, laser-based guided MoS$_2$ deposition on WS$_2$ crystal was discussed. To demonstrate improved patterning resolution and deposition selectivity, we next explore a method to selectively modify the substrate surface using electron beams before the growth.

First, we use a scanning electron microscope (SEM) to demonstrate the concept of guided MoS$_2$ growth on bare Si/SiO$_2$ substrates. Figure 5-2 (a) illustrates the process of preparing patterned MoS$_2$ without resist/mask. Parallel line patterns were first exposed by SEM line-scan mode. Pilot experiment was carried out by following our baseline MoS$_2$ CVD procedure at 795 °C (see section 2.1.2 for details) on Si/SiO$_2$ substrates pre-exposed by an electron beam (e-beam). We have observed that MoS$_2$ crystals randomly nucleate not only on the e-beam exposed lines, but also on the pristine area. Therefore, to realize selective growth, the MoS$_2$ growth process has to be further modified to suppress the MoS$_2$ nucleation at pristine area. The global nucleation and growth of MoS$_2$ on the substrate is suppressed throughout the sample by decreasing the growth temperature from 795 °C to 650 °C, which significantly improves the selectivity of MoS$_2$ nucleation.

Figure 5-2 (b) is a representative optical image of MoS$_2$ line pattern prepared by a 1 keV electron beam exposure. The nucleation and growth of MoS$_2$ were significantly promoted at the line patterns, and almost no random MoS$_2$ nucleation on the substrate was observed. The Raman E mode mapping image of the same region (Figure 5-2 (c)) confirms the preferential MoS$_2$ growth on electron-exposed substrate. As shown in the AFM image (Figure 5-2 (d)), MoS$_2$ crystals form continuous lines by nucleating along the SEM-defined line patterns. The
patterning resolution of this technique is therefore limited by MoS$_2$ grain size, not by the electron beam.

Another noticeable feature observed in Figure 5-2 (d) is that there is consistently a 10 - 15 nm tall, narrow line (indicated by the green arrows, and the cross-section profile in Figure 5-2 (e)) at the center of each MoS$_2$ line. We suggest that this is due to electron-beam-induced amorphous carbon deposition, which is confirmed by the Raman mapping and spectrum shown in Figure 5-3. The amorphous carbon, as a side product, should be removed from the sample to prevent unexpected effect on the follow-up processes for device fabrication. Based on our observation, it does not dissolve in water, ethanol and acetone at room temperature, which is likely due to the chemically bonding between amorphous carbon and the SiO$_2$ substrate. Based on our experiment results, although heating the sample in the fume hood by a hotplate to 350 °C for 2 h would partially remove the amorphous carbon, thermal profile of CVD-MoS$_2$ growth does not appear to have the same effect. This could be explained by the inert ambient of CVD furnace (growth is conducted in Ar atmosphere) so the oxygen concentration is much lower than the one in air.
Figure 5-2 Guided MoS\(_2\) growth on SEM-exposed lines. (a) Schematic illustration of resistless patterning by electron beam exposure. (b) Representative optical image and (c) Raman E mode intensity mapping image of the MoS\(_2\) line patterns, which were prepared by the SEM line-scan mode. (d) Corresponding AFM height image taken from the dashed box shown in (b). (e) Height profile extracted from the dashed line in (d).

Figure 5-3 Raman intensity mapping and spectrum of e-beam exposed lines. (a) Raman G-band intensity mapping of the amorphous carbon deposition induced by electron beam exposure in SEM. (b) Representative Raman spectra of the hydrocarbon lines (red) and Si/SiO\(_2\) background (blue).
5.4 Guided MoS$_2$ deposition on EBL exposed SiO$_2$ substrate

The line patterns in Figure 5-2 have demonstrated the concept of preferential MoS$_2$ growth using an electron beam in SEM. However, the patterns prepared by SEM are not customizable, including the pattern shape and the pattern pitch control. Moreover, as discussed in Section 5-3, it is challenging to remove the e-beam induced hydrocarbon from the substrate after its deposition. The issue of residual hydrocarbon may therefore limit its potential applications, or increase the cost for extra hydrocarbon removal process. Thus, hydrocarbon-free process for guided MoS$_2$ growth is preferred.

To demonstrate the patterning capability of MoS$_2$, and to explore other hydrocarbon-free processes, arbitrary patterns were written by an electron beam lithography (EBL) system (details see Section 2.3.3). As shown in Figure 5-4 (a)-(b), resistless, patterned MoS$_2$ was successfully prepared by following the same procedure shown in Figure 5-2 (a) with an EBL system. Because the process time for patterning is proportional to the electron exposure dose, the trade-off between process time and pattern quality needs to be addressed. Optical and AFM images in Figure 5-4 indicate that the MoS$_2$ coverage depends on the electron dose exposed on SiO$_2$ surface and MoS$_2$ nucleation density increases as the electron dose increases, as indicated by the arrows in Figure 5-4 (b). Therefore, the electron dose must be higher than a threshold to fully cover the patterned area. The layout in Figure 5-4 (a) was designed such that MoS$_2$ was grown on the same test patterns with various levels of electron dose, ranging from D (in light blue, $D = 9000 \, \mu$C/cm$^2$) to 30D (in deep blue). As shown in the AFM images (see arrows in Figure 5-4 (c)), the distribution of MoS$_2$ nucleation at 1keV patterns indicates the effective electron dose at each point of the square was not uniform. This could be explained
by the raster scanning fashion during exposure, in which the beam scanning speed was slower at the edge of the square.

Figure 5-4 1 keV test patterns for MoS$_2$ by EBL. Designed layout (a) and optical image (b) of the test patterns. Doses of the regions are D, 3D, 10D and 30D, where D = 9000 μC/cm$^2$. (c) and (d) AFM images of patterned MoS$_2$ with 10D and 30D electron dose, respectively. The corresponding areas of (c) and (d) are labeled by the orange and pink dashed boxes in (b), respectively.

To further improve the MoS$_2$ patterning resolution, the effect of beam energy on patterning quality was studied. Conventional EBL is generally operated at 30 keV energy or above to achieve higher pattern resolution (see Section 2.3.3) by suppressing the proximity effect in the resist layer. Based on the Monte Carlo simulation results depicted in Figure 5-5,
we expect that the lateral forward scattering (see arrows in Figure 5-5 (b)) of primary electrons in 300 nm SiO₂ layer can be minimized by increasing the primary electron energy, similar to the strategy used for EBL mentioned above.

Figure 5-5 Electron scattering of two electron beams with energies 6 keV and 100 keV in a SiO₂ substrate. (a) Monte Carlo simulation based on the substrate structure used in the thesis. (b) Interaction volume drawn based on (a). The red dotted line is the SiO₂/Si boundary at depth 300 nm (oxide thickness). EISS software can be accessed from 120.

A pattern with 1.5 μm pitch was designed to evaluate the quality of MoS₂ patterning (Figure 5-6 (a)). As shown in the optical image of Figure 5-6 (b), patterning at 1 keV beam energy resulted in blurred MoS₂ area boundaries, which overlap with each other. The patterning quality was improved by increasing the electron beam energy from 1 keV to 10 keV and 30 keV, as the pattern boundaries are better defined without undesirable overlapping.

Moreover, the amorphous carbon deposition was not observed in the EBL-defined patterns (see Figure 5-8 and discussion of Figure 5-9), in contrast to the MoS₂ line patterns defined by SEM (Figure 5-2). Because the base pressure of the Merlin SEM used in this work (1.3×10⁻⁶ torr) is lower than the one of Raith 150 EBL system (2.5×10⁻⁶ torr), it is unlikely that
the pressure is the driving force of the hydrocarbon deposition. Instead, based on the overall history of the two specific instruments used in this work, it is likely that the phenomenon observed in Figure 5-6 and Figure 5-8 could be explained by the lower organic contaminant concentration in the EBL chamber.

Similar to the patterned MoS$_2$ prepared by e-beam in SEM, the Raman E mode intensity mapping (Figure 5-7) and the AFM image (Figure 5-8 (b)) of MoS$_2$ patterned by EBL at 30 keV confirm the preferential MoS$_2$ growth. Pattern design and AFM images of various pattern pitches (1500 nm, 300 nm and 150 nm) are summarized in Figure 5-8. Being limited by its spatial resolution, Raman measurement is not included for patterns with pitch size smaller than 1 µm. The colors used in Figure 5-8 (a) are used to indicate from which pattern the AFM images were taken. The 30 keV MoS$_2$ pattern shown in Figure 5-8 (c) is on the verge of resolution limit, which is limited by MoS$_2$ crystal size, not by the pattern exposed by the 30 keV electron beam. As illustrated in the green pattern of Figure 5-8 (a), the designed line width is 160 nm, but the final MoS$_2$ line width (measured from the AFM image in Figure 5-8 (c)) is ~245 nm. This 53% size offset is primarily due to the MoS$_2$ crystal size (~120 nm), which is comparable to the designed line width and pattern pitch. As expected, the MoS$_2$ lines in even smaller pitch patterns (150 nm, Figure 5-8 (d)) overlapped, because the MoS$_2$ grain size is larger than the line gap (70 nm).
Figure 5.6 Beam energy effect on pattern definition. (a) Designed pattern and (b) optical images after electron exposure and CVD-MoS$_2$ growth. The test pattern pitch is 1500 nm. Electron dose was kept at 30D.

Figure 5.7 MoS$_2$ Raman E mode intensity mapping collected from the sample with 30 keV energy and 30D dose.
Figure 5-8 (a) Design of test patterns with 1500 nm (blue), 300 nm (green) and 150 nm (red) pitch. (b), (c) and (d) corresponding AFM images of test patterns with 1500 nm, 300 nm and 150 nm pitch, respectively. Electron beam energy and current are 30 keV and 30D, respectively.

To further refine the growth parameters and improve resolution, more sophisticated experimental setup with improved controllability of precursor supply for MoS$_2$ growth is required. The ideal patterning process requires deposition selectivity and patterning resolution. To improve the patterning resolution, the MoS$_2$ grain size has to be smaller, which implies shorter growth time and/or slower growth rate. The growth time for MoS$_2$ patterning (7 min) is just enough for the sulfur powder to evaporate and to transfer from the sulfur boat to the substrate. If the growth time is 5 min, there is no growth observed on the sample. MoS$_2$ growth rate, as discussed in section 4-3, is suppressed by decreasing the growth temperature to 650 °C, which is just sufficient for observable, selective MoS$_2$ growth. There is no growth observed on the sample if the growth temperature is 625 °C. In our experimental setup, the substrate and the precursor (MoO$_3$) are placed in the same temperature zone, which means that the substrate temperature is convoluted to the supply of MoO$_3$ and sulfur precursor. Therefore, growth equipment with deconvoluted parameters (Mo-precursor supply, S-precursor supply, substrate
temperature, and growth time) is beneficial for wider process window under constraints of guided growth discussed above.

5.5 Characterization after e-beam exposure

To investigate the underlying mechanism of preferential MoS$_2$ growth, the samples with electron beam exposure before and after CVD-MoS$_2$ deposition were further analyzed. As discussed in the previous section, the “ridges” observed in Figure 5-2 (d) are likely carbon-based deposition due to the contamination in the SEM chamber$^{74,103,104}$. Heterogeneous nucleation around the amorphous carbon may play a role in the observed selective deposition, but it does not appear to be necessary for preferential MoS$_2$ growth on the patterns prepared by EBL tool. To illustrate, AFM images in Figure 5-9 (a)-(d) were collected right after electron beam (30 keV) exposure on bare Si/SiO$_2$ substrate. Based on the AFM tapping mode images in Figure 5-9, no trace of amorphous carbon on the surface was observed. In contrast, these AFM images consistently showed similar trench-like features (dips in the surface), indicating apparent removal of the material during e-beam irradiation. However, because SiO$_2$ sputtering by the electron beam in vacuum is unlikely in our experimental conditions, these AFM features cannot be ascribed to thickness/height variations, and other parameters that influence tip-sample interaction must be considered.

The tip-sample interaction is governed by both attractive and repulsive forces whose strength is distance-dependent and also relies on both sample surface and the tip used for imaging (more discussion of AFM principles in Section 2.2.2). In case of charge-neutral
surfaces, AFM images can be ascribed to morphological/surface features. However, the apparent trenches observed in our measurements indicate that there are other non-uniformities in addition to SiO$_2$ surface morphology. The trench-like artifacts indicate attractive interaction between the SiO$_2$ surface and the AFM tip. Furthermore, the apparent depth of the “trenches” is summarized in Figure 5-9 (e)(f), showing that the apparent depth increases as the electron dose increases, which further indicates that the effect is charge-related. Due to the ejection of secondary and backscattered electrons, incident electron beam (30 keV) introduces positive charge trapped in the insulating layer$^{71}$, with most of the primary electrons leaving the sample by being grounded from Si substrate. As discussed in Section 2.3.1, if the electron energy is sufficient to penetrate the sample, then the sample is positively charged. To evaluate the electron range in 300 nm SiO$_2$ layer, Monte Carlo simulation of electrons with various energies (1 keV - 100 keV) was performed. As shown in Figure 5-10 (e), most of the primary electrons (30 keV) could penetrate SiO$_2$ and be grounded.

![Figure 5-9 “Trench” artifacts observed in AFM images of e-beam charged SiO$_2$ surface. (a)-](image)

Figure 5-9 “Trench” artifacts observed in AFM images of e-beam charged SiO$_2$ surface. (a)-
(d) AFM images collected after 30 keV electron exposure with dose 10D, 30D, 50D and 100D respectively, where D = 9000 μC/cm² 
(e) Apparent height profile extracted from AFM images in (a)-(d). 
(f) Dependence of apparent trench depth to corresponding electron dose. The dotted line is a guide to the eye for the trend.

![AFM images](image)

Figure 5-10 Monte Carlo simulation results of electrons with various energies landing SiO₂ sample. The red dotted line is the SiO₂/Si boundary at depth 300 nm (oxide thickness). Scale bar in (a) applies to all panels. EISS software can be accessed from 120.

After the electron beam exposure, the decay of charge in the SiO₂ layer is negligible, for a gigantic charge decay time constant, \( \tau = 215 \) days, which can be evaluated by Equation 5-171,

\[
\tau = \rho \varepsilon_r \varepsilon_0
\]

where \( \rho \), \( \varepsilon_r \), and \( \varepsilon_0 \) are resistivity of SiO₂ (7×10¹⁷ Ω-m), dielectric constant of SiO₂ (3.9), and vacuum permittivity (8.85×10⁻¹² F/m), respectively. This is confirmed by the fact that the AFM
measurement result is virtually the same as the images shown in Figure 5-9 (a)-(d) 40 days after the electron exposure.

To characterize the charging phenomena in SiO$_2$ substrates exposed by electron beam, surface potential images are collected by scanning Kelvin probe microscopy (SKPM discussed in more details in Section 2.2.3) technique. In addition to probing the work function contrast, SKPM has been used to analyze the charges trapped in dielectrics $^{121,122}$. To quantify the surface potential and verify the simulation result discussed above, samples exposed by a 100 keV electron beam are prepared and analyzed. An isolated $5 \mu m \times 5 \mu m$ area was exposed by a 100 keV electron beam, with dose at 100D, where $D = 9000 \mu C/cm^2$. The SKPM images along with the surface topography of both SiO$_2$ and bare Si samples are summarized in Figure 5-11. As illustrated in the SiO$_2$ height profile (Figure 5-11 (a)), an apparent “well” with depth about 2 nm is observed, agreeing the height images in Figure 5-9. The surface potential image in Figure 5-11 (b) indicates that the SiO$_2$ is positively charged after electron exposure, which induces a potential difference $\Delta V_{SiO_2} = +27$ mV. This result agrees well with our prediction and discussion in Figure 5-9, as the primary electrons used in Figure 5-11 (100 keV) is also sufficient to arrive the p-type Si substrate through the 300 nm oxide. The contrast of the surface potential is solely from the charging effect, because we are probing the work function of SiO$_2$ with and without electron exposure. Moreover, the surface potential contrast of the SiO$_2$ sample remained unchanged even after being kept in air for 14 days, which is not surprising because the charge could be trapped in the bulk of SiO$_2$ (300 nm thick) without being grounded or neutralized.
Topography (Figure 5-11 (b)) and surface potential (Figure 5-11 (d)) images of bare Si indicate that charging effect is suppressed when there is no thick oxide to sustain the static charge after electron beam exposure. Before the measurement, same electron exposure parameters were applied for bare Si as for SiO$_2$. Neither trace of carbon deposition or apparent “well” are observed in the topography of bare Si sample (Figure 5-11 (d)). Moreover, the surface potential difference $\Delta V_{Si}$ (7 mV) measured from the image in Figure 5-11 (e) is much lower than the one measured from SiO$_2$ (27mV). Modulating the energy barrier of chemical reactions by electric field has been predicted theoretically$^{123-125}$ and realized experimentally$^{126}$.

Based on the observation and discussion in Sections 5.3 and 5.4, electrostatically induced guiding is suggested as the mechanism driving the preferential MoS$_2$ deposition on electron beam exposed SiO$_2$ substrate.

Figure 5-11 (a) Topography and (b) surface potential images of SiO$_2$ after 100D electron beam exposure; (d) Topography and (e) surface potential images of bare Si after 100D electron beam exposure. (c) and (f) location of electron exposure in corresponding SiO$_2$ and Si samples, respectively. The tip height is 50 nm above the sample surface during Scanning Kelvin
measurement (nap mode).

Figure 5-12 Cross-section surface potential profile of the corresponding dash lines in Figure 5-10. SiO$_2$: blue curve collected from Figure 5-10 (b); Si: red curve collected from Figure 5-10 (e).

**Discussion**

In Section 5.5, we have suggested that the surface potential contrast observed in Figure 4-10 originates from trapped static charge in SiO$_2$. In this section, other possibilities are presented and discussed. For instance, electron beam with high energy and high dose could heavily damage SiO$_2$, forming amorphous silicon (a-Si) cluster. Based on the electron energy loss spectroscopy (EELS) data and annular dark field (ADF) images, oxygen atoms in SiO$_2$ are selectively depleted by e-beam exposure in a transmission electron microscope (TEM)\textsuperscript{127}. In this case, the work function of the sample is therefore locally modulated by e-beam induced damage. However, the electron beams used in our work are unlikely to modify the SiO$_2$ composition, because the beam parameters (beam energy \(\leq 100\) keV, electron dose \(\leq 9\times10^3\) C/m$^2$) are well below the threshold (beam energy 100 keV, electron dose $10^5$ - $10^7$ C/m$^2$) of converting SiO$_2$ into a-Si.
5.6 Conclusion

In conclusion, we demonstrated two resistless methods for guided MoS$_2$ growth by treating the substrates locally. The concept was first demonstrated by exposing a laser beam on an ex-WS$_2$ crystal. The preferential MoS$_2$ growth at the lines was observed, but the deposition selectivity and the pattern resolution of MoS$_2$ require significant improvement for potential applications. We then move on to electron beam exposure for selective substrate treatment. The guided MoS$_2$ growth by electron beam exposure was observed in the Si/SiO$_2$ samples prepared across multiple scanning electron beam systems, in which we found improved patterning resolution under higher beam energy during exposure, accompanying higher selectivity than laser-based approach. In addition, we discovered that the carbon-induced preferential nucleation is not necessary for resistless patterning. The role of static charge of the resistless patterning technique is further confirmed by the SKPM results after e-beam exposure. We have also found that the thick SiO$_2$ layer is needed for the static charge retention. The resistless technique significantly simplifies the patterning process for CVD-MoS$_2$ and it has potential for patterning other material system in general.
Chapter 6 Conclusions and Outlook

6.1 Conclusions

In this thesis, we have developed the resist-free, guided TMD growth and etching processes, followed by investigating the underlying mechanisms of laser-based and e-beam based processes, which solve the processing issues and significantly improve the process productivity.

The thesis begins with an overview of recent research trend of regarding 2D materials, specifically, TMD materials. The potential applications include RED membranes for energy harvesting, HER material for energy conversion and storage, and channel material for future FET devices. The motivation of this thesis is then addressed by pointing out the drawbacks of conventional lithography processes, and the reason why it is desirable to develop dedicated processes for 2D material patterning.

In Chapter 3, guided MoS$_2$ decomposition is demonstrated by defect engineering followed by annealing MoS$_2$ in air, and electron exposure prior to nanopore formation. We first investigated the oxidative nanopore formation in CVD-MoS$_2$ crystals annealed in air. A nanopore nucleation model was then proposed: the minority defects (defect species other than V$_s$) in MoS$_2$ govern the nucleation process.

In Chapter 4, electron beam exposure was then used to modulate the nanopore density in
MoS$_2$. This process opens avenues for controlling nanopore density in MoS$_2$, potentially in other TMD materials as well. We demonstrate that material modification through defect engineering prior to the pore formation is a promising direction for the nanopore density control for future 2D membrane applications. The oxidative annealing process can be used as a defect diagnostics tool for rapid materials control. We have also demonstrated the defect introduction by laser exposure on mechanically exfoliated WS$_2$ crystals, which were found effective as MoS$_2$ nucleation template for heterostructure preparation.

In Chapter 5, we demonstrated two resistless methods for guided MoS$_2$ growth by treating the substrates locally. The concept was first demonstrated by preferential MoS$_2$ growth at the laser-exposed lines, but the deposition selectivity and the pattern resolution of MoS$_2$ limit its applications. We then move on to electron beam exposure for guided substrate treatment. The guided MoS$_2$ growth by electron beam exposure was observed in the Si/SiO$_2$ samples prepared across multiple scanning electron beam systems, in which we found improved patterning resolution under higher beam energy during exposure, accompanying higher selectivity than laser-based approach. In addition, we discovered that the carbon-induced preferential nucleation is not necessary for resistless patterning. The role of static charge of the resistless patterning technique is further confirmed by the SKPM results after e-beam exposure. We have also found that the thick SiO$_2$ layer is needed for the static charge retention. The resistless technique significantly simplifies the patterning process for CVD-MoS$_2$ and it has potential for patterning other material system in general.
6.2 Future works

In Chapter 3, we discussed the role of majority and minority defects in nanopore nucleation in MoS$_2$, assuming that the defects are charge neutral. Nevertheless, the defect species mentioned in Figure 3-8 could act as a charge trapping sites, forming charged defects in MoS$_2$ due to its n-type semiconductor nature. Although it may be challenging to characterize individual charged defects experimentally, one could use first-principle simulation to predict if the point defects are more stable with trapped charge(s). Both negatively and positively charged defect species have been predicted and studied$^{128,129}$. Based on their prediction, however, it is not conclusive if the formation energies of charged defects are lower or higher than the corresponding neutral defects. To explore the role of charged defects in TMD pore formation, more rigorous theoretical studies are therefore desirable.

In Section 4.2, we have demonstrated guided MoS$_2$ removal by electron beam exposure prior to annealing MoS$_2$ crystals in air. We expect this approach to work in other 2D materials, such as WS$_2$ and graphene. By consistently controlling the conditions of material growth and electron exposure, the treatment can be used to modulate both the density and the size of the nanopores in 2D membranes. Finally, MoS$_2$ (or other 2D materials) with controllable nanopores can be applied in membrane-based devices and catalysis surface for hydrogen evolution reaction.

Moreover, one could design the electron exposure conditions such that the decomposition selectivity is maximized: 100% material removal at the exposed areas, while 0% material removal at the pristine areas after being annealed in air. SEM image shown in Figure 6-1 is
taken from another MoS$_2$ crystal from the same sample shown in Figure 3-6 (c). The electron
dose in the high dose area is $6.4 \times 10^{18}$ cm$^{-2}$, 8 times higher than the one in Figure 3-6 (c), while
the dose in low dose area in Figure 6-1 is not quantifiable because the area was exposed during
beam tuning (focus and stigmator alignment). One can therefore apply this concept for
resistless, guided removal of other material systems.

Figure 6-1 Complete, guided MoS$_2$ removal by electron exposure followed by annealing in air.

The concept of resist-free, guided MoS$_2$ deposition discussed in Chapter 4 should be
applicable to other TMD systems (MX$_2$) and beyond, especially for processes involving
precursor molecules with polar properties. For instance, molecules of self-assembly
monolayers (SAM) with polar/non-polar head group. If the substrate is locally modulated by
static charge, the positive/negative patterned SAM deposition could be realized. Deposition
selectivity of different functional groups at areas with various electron dose have to be studied.

As discussed in Section 5.4, to improve the patterning resolution, growth equipment with
deconvoluted process parameters (Mo-precursor supply, S-precursor supply, substrate
temperature, and growth time) is beneficial for wider process window under constraints of guided growth. Such equipment is also promising for further improving the deposition selectivity, which is crucial for device applications. Therefore, wider range of precursor choice and improved equipment design should be explored in the future.

Charge deposition by corona discharge\textsuperscript{130–133} has been utilized for characterizing the band bending and interface charge states in oxide–semiconductor structure. The simple setup of corona discharge provides an even lower cost, high throughput alternative option. The treatment, however, is macroscopic, so a protective mask or prepatterned photoresist layer is required to prepare patterned charged surface. Due to the low kinetic energy of charged ions deposited by corona discharge, the static charge is concentrated at sample surface. The charge decay, especially when being exposed in humid ambient, could be an issue to address during process optimization.

In addition to its imaging mode, helium ion microscope (HIM) can also be used for SiO\textsubscript{2} substrate exposure prior to MoS\textsubscript{2} deposition. We have confirmed that helium ion exposure is effective in inducing guided MoS\textsubscript{2} growth, based on our preliminary results. Helium ions carry positive charge, and the ions induce more positive charge in the substrate by ejecting secondary electrons and back-scattered electrons with much higher yield than electron beams with the same beam energy. With its high beam current and higher electron yield, helium ion exposure is expected to have higher throughput because shorter exposure time is required. Furthermore, HIM can be easily upgraded to pattern preparation equipment, using the same concept as EBL. Customized pattern preparation by HIM-based equipment is therefore easily
achievable, and the corresponding study regarding HIM-induced guided growth in the future is suggested. All other charged beams in general are therefore expected to be effective in guiding MoS$_2$ growth, but ion-induced substrate sputtering by heavy ion species could be an issue if the substrate flatness and/or roughness are critical.
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